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MEMORIAL LECTURES

THE TRANSURANIUM ELEMENTS

by GLENN T. SEABORG

UNIVERSITY OF CALIFORNIA

BERKELEY, CALIFORNIA

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Preface

THE FOUR CHAPTERS of this volume bear the same titles as the individual Silliman Lectures which I had the pleasure of giving at Yale University in May 1957. In writing up these lectures for publication I find that I have expanded the material so considerably that the chapters bear only a formal relationship to the lectures as originally presented.

The historical material in this book is in many respects a personal recollection, and this is especially true of Chapter 1. I have chosen not to give detailed documentation to the original literature, as this volume is not intended for the specialist; such references as I do supply are mainly citations of names. This is particularly appropriate in Chapter 1, since much of the historical narrative material was never set down in published form. I am sure that many people who deserve to be included have been overlooked; I can only hope that such inadvertent omissions will be accepted with indulgence by any readers who have been treated so unjustly.

There is much historical material in this book. Descriptions of the discoveries of each of the transuranium elements are woven, I hope in a natural way, into the various chapters. Pictures are included of the first pure samples of neptunium, plutonium, and curium and of one of the earliest samples of americium to be isolated. The original discovery experiments are described in some detail, and the exact date of the crucial break-through discovery experiment is included for each transuranium element, insofar as this is possible. The transcurium elements were all chemically identified first in ion-exchange adsorption-elution experiments, and the original elution curve is included in each case.

Although Chapter 1 bears the broad title "The Plutonium Story," it should be admitted that the emphasis is on the scientists on the laboratory level who actually handled plutonium in one way or another. This means that much emphasis is placed on

chemists, whose contributions were largely overlooked in the famous Smyth Report. Little emphasis is placed on the important contributions at the administrative level; for an excellent narrative account which includes an authoritative review of the Plutonium Story from this point of view I recommend A. H. Compton's book *Atomic Quest*.

Numerous colleagues, present and past, have helped in the reconstruction of the events which are reviewed in Chapter 1. I owe a special debt of gratitude to my colleague B. B. Cunningham, who played such a prominent role in this development; he gave generously of his time in assisting to construct the account that finally evolved as Chapter 1. An unpublished account of the evolution of the Bismuth-Phosphate Process by G. W. Watt and S. G. Thompson served as a very helpful source of information and as a basis for the corresponding section in this chapter. I also want to express my thanks to the following, each of whom read part or all of this chapter and gave me valuable suggestions from their memories of the roles they played in this historic venture: L. W. Alvarez, G. E. Boyd, J. E. Cole, R. E. Connick, V. R. Cooper, C. D. Coryell, B. B. Cunningham, R. M. Evans, S. Fried, F. T. Hagemann, B. G. Harvey, H. H. Hyman, L. I. Katzin, A. S. Langsdorf, Jr., W. M. Manning, A. S. Newton, L. C. Peery, I. Perlman, E. Segrè, L. Squires, S. G. Thompson, A. C. Wahl, J. E. Willard, L. Winsberg, and H. D. Young.

Chapter 2 goes beyond the limits implied by the title of the book in that the chemistry of all of the actinide elements, including the heaviest natural elements—thorium, protactinium, and uranium—is treated. It is a difficult assignment to make a meaningful summary of the chemical properties of the entire actinide group of elements short enough to be consistent with the objective of the book, which is the presentation of a reasonably brief over-all survey of the transuranium elements. I chose to treat the actinide elements in a correlative fashion, a method that makes it possible to cover most efficiently many distinctive properties that are common to many of these elements; this method also has the advantage of emphasizing the unique and interesting character of this series of elements. The task of writing this chapter was considerably lightened as the result of my collaboration with my friend J. J. Katz on

our recently published comprehensive book *The Chemistry of the Actinide Elements*. Valuable material for this chapter was furnished by B. B. Cunningham, B. G. Harvey, E. K. Hyde, and J. C. Wallmann, my colleagues at the Radiation Laboratory, and by M. S. Fred of the Argonne National Laboratory.

The selection of material was perhaps most difficult of all for Chapter 3. The available nuclear information on the transuranium elements is so extensive and the treatment of it so complicated that it was difficult to arrive at what seemed to be a proper compromise to meet the objective of this book. B. M. Foreman, Jr., made a major contribution to this chapter by carrying out the extensive calculations of the masses of the nuclides and by helping with the preparation of the figures which summarize the decay cycles and the systematics of radioactive decay. I was particularly fortunate in having the aid of two visitors to our laboratory, S. G. Nilsson and J. O. Newton, and of my colleague, J. O. Rasmussen, all of whom not only helped in the preparation of material but served as my instructors in the intricacies of the unified model of the nucleus. Another member of our laboratory, W. J. Swiatecki, helped me in a similar fashion in the sections that deal with the fission process. I also owe a special debt of gratitude for aid on many aspects of this chapter to my colleague E. K. Hyde and also to F. Asaro, H. R. Bowman, G. E. Gordon, B. G. Harvey, J. M. Hollander, B. W. Hoff, E. K. Hulet, T. D. Thomas, and R. Vandenbosch.

Much of Chapter 4 ("Future Synthetic Elements") is, I fear, written in a fanciful vein. Many predictions of the chemical and nuclear properties of undiscovered transuranium elements are attempted. These cannot be very exact, but I could not resist the temptation to indulge in this delightful game. It should be interesting to see the changes that future editions, if any, will find in this chapter. L. Brewer, B. B. Cunningham, B. M. Foreman, Jr., A. Ghiorso, B. G. Harvey, E. K. Hyde, S. G. Thompson, and J. C. Wallmann gave aid here but must not, of course, accept responsibility for any of the guesses which the future will reveal as having been far from correct. It is inevitable that many of these predictions will prove to be wrong.

D. Strominger and B. M. Foreman, Jr., helped in the compila-

tion of the table of radioactive properties which is included in the Appendix, and Mrs. Elinor Potter and Miss Eileen Carson aided in the preparation of the name and subject indices. I want to express particular appreciation for the invaluable aid given by Miss Carson, who served as a technical assistant in the preparation of the entire manuscript.

It seems to be impossible to prepare a book on the transuranium elements that is up to date with respect to the number of known transuranium elements at the time of issue. Our book *The Transuranium Elements: Research Papers* (Volume 14B of the National Nuclear Energy Series) was short by two elements which were discovered while the book was in press. Similarly, our later book *The Actinide Elements* (Volume 14A in the same series) failed to include another two elements for the same reason. *The Chemistry of the Actinide Elements* apparently erred in the opposite direction; an account of the apparent discovery of an element was added in the proof stage with the unexpected result that the book included one element whose discovery was extremely doubtful by the time of its issue.

The discovery of an isotope of element 102, reported to decay by the emission of 8.5 ± 0.1 Mev alpha particles with a half life of about 10 minutes and to be produced by the bombardment of curium with approximately 90-Mev C^{13} ions, was announced last summer by an international group of scientists and was included as mentioned. Unfortunately, since this announcement no additional data have been obtained to support this discovery, in spite of a very long and careful series of experiments in our own laboratory, undertaken with the advantage of apparently more than adequate facilities. To complicate this form of journalism still further, just last month a group in our laboratory succeeded in identifying the isotope 102^{254}—decaying by the emission of alpha particles with the half life of ~3 seconds and produced by the reaction Cm^{246} (C^{12}, 4n)—through the chemical identification of the known daughter 30-minute (7.43-Mev alpha emitter) Fm^{250} separated by recoil from its alpha-decaying parent. Thus because of a loss of confidence in the validity of the earlier work and because the results of last month came too late, the text of this book, upon publication, will be lacking a discussion of element 102 as a known element. Whether

or not further deficiencies of this kind will be built into this book while it is in press, I do not know; but I feel quite confident that it is destined, in the not too distant future, to be further out of date in this respect.

I appreciate the fine hospitality which was extended me during my stay at New Haven; I am even more grateful for the incentive to write what might otherwise never have been written, since much of the historical material in the book might easily have been lost. In fact, I found that the lapse of time, and in some cases the near disappearance of original data made the task extremely difficult; a further delay might well have made it impossible.

Berkeley, California GLENN T. SEABORG
May 1958

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. . . surely to alchemy this right is due, that it may be compared to the husbandman whereof Aesop makes the fable; that, when he died, told his sons that he had left unto them gold buried underground in his vineyard; and they digged over all the ground, and gold they found none; but by reason of their stirring and digging the mould about the roots of their vines, they had a great vintage the year following: so assuredly the search and stir to make gold hath brought to light a great number of good and fruitful inventions and experiments.

FRANCIS BACON, *The Advancement of Learning*

Chapter 1. The Plutonium Story

THE story of plutonium is one of the most dramatic in the history of science. For many reasons this unusual element holds a unique position among the chemical elements. It is a synthetic element, the first realization of the alchemist's dream of large-scale transmutation. It was the first synthetic element to be seen by man. One of its isotopes has special nuclear properties which give it overwhelming importance in the affairs of man. It has unusual and very interesting chemical properties. It is one of the most dangerous poisons known to man. It was discovered and methods for its production were developed during the last war, under circumstances that make a fascinating and intriguing story. It is, of course, a continuing story, and added chapters will have to be written at a later date.

In view of plutonium's position as one of the transuranium elements, its story must be interwoven with theirs. Thus this discussion of plutonium in Chapter 1 will include some consideration of several of the earlier transuranium elements, with the heavier elements in this group to be introduced in the following chapters.

The search for transuranium elements, a quest born of scientific curiosity, was destined to be the trigger for a series of events which, within a decade, were to rock the world and burst upon the consciousness of every literate human being. These events were the discoveries that led to the exploitation of nuclear energy, particularly as a weapon of mass destruction. Other fundamental scientific discoveries in the past undoubtedly have had an equal, if not greater, effect on man's mode of existence, but no other exploded in his face as has this one: the announcement to the world of the existence of plutonium was in the form of the nuclear bomb dropped over Nagasaki.

1.1 The Beginning and Neptunium

One can choose as a beginning for the story of the transuranium elements the discovery in 1934, by E. Fermi, E. Amaldi, O. D'Agostino, F. Rasetti, and E. Segrè, that neutron irradiation of uranium leads to a considerable number of radioactive substances. The chemical investigation of these radioactivities led, however, to discovery of the fission process rather than of the transuranium elements. In their original work Fermi and his co-workers were led, on the basis of chemical experimentation, to assign these radioactivities to transuranium elements. The work of O. Hahn, L. Meitner, F. Strassmann, and others appeared at first to confirm this point of view, and for several years the "transuranium elements" were the subject of much experimental work and discussion. However, early in 1939 Hahn and Strassmann described experiments which made it certain that they had observed radioactive isotopes of barium and other "light" elements as the result of the bombardment of uranium with neutrons. Subsequent work showed that practically all of the radioactivities previously ascribed to transuranium elements were actually due to fission products.

With poetic justice, the actual discovery of the first transuranium element in turn resulted from experiments aimed at understanding the fission process. Several experimenters, including E. M. McMillan of the University of California, measured the energies of the two main fission fragments by observing the distances they traveled from each other as a result of their mutual recoil when the nucleus explodes. McMillan noted that there was another radioactive product of the reaction, with a half life of 2.3 days, which did not recoil, at least not sufficiently to escape from the thin layer of fissioning uranium. He suspected that this was a product formed by simple neutron capture—a process which does not release much energy—rather than by fission. In the spring of 1940 McMillan and P. H. Abelson deduced by chemical means that this product is surely an isotope of element 93, arising by beta decay from U^{239}. The U^{239} has a half life of 23 minutes. Element 93 was given the name neptunium (Np) because it was beyond uranium, just as the planet Neptune is beyond Uranus.

McMillan's and Abelson's tracer investigations of the chemical properties of neptunium showed that it resembles uranium, and does not resemble rhenium, in its chemical properties. This was the first definite recognized evidence that the 5*f* electron shell undergoes filling in this region. Thus the discovery of neptunium was extremely important, not only from the standpoint of opening the transuranium field but also as the break-through to an eventual understanding of the electronic structure and the place in the periodic system of the heaviest elements.

The discovery of the fission of uranium in the chemical experiments of Hahn and Strassmann late in 1938 was followed within a month or two by confirmatory physical (ionization chamber) experiments in numerous laboratories in the United States and Europe. Early in 1940 it was demonstrated by A. O. Nier, E. T. Booth, J. R. Dunning and A. V. Grosse that, as N. Bohr predicted, it is the rare isotope U^{235} which undergoes fission—a result of great importance to the production of a chain reaction in natural uranium. The possibility of producing such a chain reaction depended critically on whether neutrons are emitted during the fission process and upon the number emitted. The important information that two or three neutrons are emitted whenever a uranium nucleus undergoes fission was obtained early in 1939 in the experiments of L. Szilard and W. H. Zinn and also of H. L. Anderson, Fermi, and H. B. Hanstein, all at Columbia University, and in the essentially simultaneous experiments of H. von Halban, F. Joliot, and L. Kowarski working in Paris. Thus it was already clear that a nuclear chain reaction in uranium enriched in U^{235} was a possibility, and the answer to the question of whether such a possibility existed for natural uranium depended on the exact values of neutron cross sections involved. Important to the control of the chain reactor was the discovery in 1939 by R. B. Roberts, L. R. Hafstad, R. C. Meyer, and P. Wang that some tenths of one per cent of the fission neutrons are emitted a few seconds after the fission occurs.

1.2 Discovery and Early Investigations of Plutonium

The discovery of plutonium should be described in some detail. In the fall of 1940 I asked a graduate student, A. C. Wahl, to consider the possibility of studying the tracer chemical properties of element 93 as a thesis problem, a suggestion which he was happy to accept. This, and related work on element 94, was carried on in collaboration with J. W. Kennedy, who, like myself, was at that time an instructor in the Department of Chemistry at the University of California. After McMillan's departure from Berkeley in November 1940, and his gracious assent to our continuation of the work he had begun on the search for and possible identification of element 94, our group turned its major efforts to this problem.

Our first bombardment of uranium oxide with the 16-Mev deuterons from the 60-inch cyclotron was performed on December 14, 1940. Alpha radioactivity was found to grow into the chemically separated element 93 fraction during the following weeks, and this alpha activity was chemically separated from the neighboring elements, especially elements 90 to 93 inclusive, in experiments performed during the next two months. These experiments, which constituted the positive identification of element 94, showed that this element has at least two oxidation states, distinguishable by their precipitation chemistry, and that it requires stronger oxidizing agents to oxidize element 94 to the upper state than is the case for element 93. The first successful oxidation of element 94, which probably represents the key step in its discovery, was effected through the use of peroxydisulfate ion and silver ion catalyst on the night of February 23–24, 1941, in a small room (No. 307) on the third floor of Gilman Hall on the University of California campus in Berkeley. The particular isotope identified has been shown to be of mass number 238, and the reactions for its preparation are as follows:

$$_{92}U^{238} + {}_{1}H^{2} \longrightarrow {}_{93}Np^{238} + 2n$$

$$_{93}Np^{238} \xrightarrow[2.1\ \text{days}]{\beta^-} {}_{94}Pu^{238}\ (86\ \text{years},\ \alpha).$$

In view of its apparent importance, the announcement of this discovery was withheld by the discoverers and the editors of the

Physical Review as the result of self-imposed secrecy, even though this work antedated the time of governmental support. It may be of interest to reproduce here the letters to the editor which were submitted for publication in the *Physical Review* but held in custody by one of their editors until publication after the war, in 1946. The text of a communication dated January 28, 1941, read as follows:

We are writing to report some results obtained in the bombardment of uranium with deuterons in the 60-inch cyclotron.

The uranium was bombarded in the form of U_3O_8 and the deuterons had to pass through a 2-mil thickness of aluminum foil before hitting the uranium target. The carefully purified element 93 fraction contained a beta-activity whose aluminum absorption curve (taken on an ionization chamber connected to a FP-54 tube and also on a Lauritsen electroscope) was distinctly different from the absorption curve of a sample of the 2.3–day 93^{239} (formed from uranium plus neutrons) taken under identical conditions. The upper energy limit of the beta particles from this new 93 activity is about 1 Mev, compared with about 0.5 Mev for 93^{239}. The ratio of gamma-ray to beta-particle ionization is about five times larger than for 93^{239}. The initial part of the absorption curve of this 93 from uranium plus deuterons is very similar to the initial part of the absorption curve of 93^{239}. Of course the production of 93^{239} is expected in the deuteron bombardment of uranium, from the reaction $U^{238}(d,n)93^{239}$. It is impossible to deduce from the absorption curve the relative intensities of the new 93 and of 93^{239}, since the initial parts of the individual absorption curves of these two activities might well be nearly identical. The rate of decay of the high energy beta-particles (0.5—1 Mev) and gamma-rays from the 93 of uranium plus deuterons was determined. This gave a half-life of about 2 days for the new 93. This activity is probably to be assigned to 93^{238}, 93^{236}, or 93^{235} formed in the reaction $U^{238}(d,2n)93^{238}$, $U^{235}(d,n)93^{236}$, or $U^{235}(d,2n)93^{235}$, respectively.

The growth of alpha-particles, which might be due to the element 94 daughter of the 2-day 93, was then looked for. We did observe the growth of alpha-particles in the very carefully purified, as well as in the semi-purified 93 fractions, and the growth curves indicate a half-life of roughly 2 days for the parent of the alpha-emitter. The final alpha-particle count amounts to several hundred counts per minute for a bombardment of 200 microamperehours. This work was done with a proportional type counter. We plan to redetermine the alpha-particle growth curve more accurately, using an ionization chamber and linear amplifier with the help of a magnetic field to bend out the very strong beta-particle background. The alpha-particles have a range of approximately 3.9 cm in air.

This alpha-activity is chemically separable from uranium and 93. The chemical experiments so far indicate a similarity to thorium and the ac-

tivity has not yet been separated from thorium. More chemical experiments definitely must be performed before it can be regarded as proved that the alpha-particles are due to an isotope of element 94.

The report dated March 7, 1941, on the oxidation experiment which occurred on February 24, 1941, read as follows:

We should like to report a few more results which we have found regarding the element 94 alpha-radioactivity formed in the 16-Mev deuteron bombardment of uranium. We sent a first report of this work in a Letter to the Editor of January 28, 1941. We have in the meantime performed more experiments in order to study the chemical behavior of this alpha-radioactive isotope. The radioactivity can be precipitated, in what is probably the +4 valence state, as a fluoride or iodate by using a rare earth or thorium as carrier material and as a peroxyhydrate by using thorium as carrier material. However, in the presence of the extremely strong oxidizing agent persulfate ion ($S_2O_8^{=}$), plus Ag as a catalyst, this radioactive isotope is oxidized to a higher valence state which does not precipitate as a fluoride. The oxidizing agent bromate ion (BrO_3^-) is not sufficiently powerful to oxidize it to this higher valence state and hence the radioactivity comes down as a fluoride even in the presence of bromate ion. With the help of persulfate ion it has been possible to separate quantitatively this radioactivity from thorium, by using the beta-active UX_1 as an indicator for thorium. These experiments make it extremely probable that this alpha-radioactivity is due to an isotope of element 94. The experiments are being continued.

The chemical properties of elements 93 and 94 were studied by the tracer method at the University of California for the next year and a half. These first two transuranium elements were referred to by our group simply as "element 93" and "element 94," or by code names, until the spring of 1942, at which time the first detailed reports on them were written. The early work, even in those days, was carried on under a self-imposed cover of secrecy—as a matter of fact, I recall that a code name was often used for element 94, even in oral references. Throughout 1941 we referred to it by the code name of "copper," which was all right until we found it necessary to introduce the element copper into some of our experiments; we were then faced with the problem of distinguishing between the two. For a while we referred to plutonium as "copper" and the real copper as "honest-to-God copper." This seemed clumsier and clumsier as time went on, and we finally christened the

element "plutonium" and began to call it that. In order to write the original report on the chemical properties, it became necessary to have chemical symbols for the two elements.

This report, by A. C. Wahl and myself, dated March 19, 1942, was mailed as a secret report from Berkeley, California, to the Uranium Committee (the group, headed by L. J. Briggs, that had been coordinating the early United States work on possible practical energy from nuclear fission) in Washington, D.C., and it was issued as Report No. A-135. Although it was published in its original form after the war, it may be interesting to quote the section in which the name plutonium was first suggested:

> *Naming the Elements.* Since formulas are confusing when the symbols "93" and "94" are used, we have decided to use symbols of the conventional chemical type to designate these elements. Following McMillan, who has suggested the name "neptunium" (after Neptune, the first planet beyond Uranus) for element 93, we suggest "plutonium" (after Pluto, the second planet beyond Uranus) for element 94. The corresponding chemical symbols would be Np and Pu. The names "eka-rhenium" and "eka-osmium" seem inappropriate in view of the marked dissimilarity of the chemical properties of elements 93 and 94 to those of rhenium and osmium.

As a result of these tracer investigations during 1941 and early 1942 at the University of California, to which Wahl made the major contributions, a great deal was learned about the chemical properties of plutonium. It was established that it had at least two oxidation states, the higher of which was not carried by lanthanum fluoride or cerium fluoride, while the lower state was quantitatively coprecipitated with these compounds. It was established that the higher oxidation state could be obtained by treatment of the lower state with oxidizing agents such as persulfate and argentic ions, dichromate, permanganate, or periodate, and that the upper state could be reduced to a lower (rare earth fluoride-carriable) state by treatment with sulfur dioxide or bromide ion. The approximate oxidation-reduction potential of the couple plutonium (reduced) $\rightarrow$ plutonium (oxidized) was believed to be between -1.0 and -1.4 volts. It was established that plutonium in aqueous solution is not reduced to the metal by zinc, and that plutonium does not form a volatile tetroxide. It was shown that a stable lower state of plu-

tonium—probably plutonium (IV)—was carried by $Th(IO_3)_4$. Ether extraction had been used to separate large amounts of uranyl nitrate from plutonium. Methods had also been devised for the separation of plutonium from elements 90, 91, and 93.

On the basis of these facts and others not mentioned here, it was speculated that plutonium in its highest oxidation state is similar to uranium (VI) and in a lower state is similar to thorium (IV) and uranium (IV). It was reasoned that if plutonium existed normally as a stable plutonium (IV) ion, it would probably form insoluble compounds or stable complex ions analogous to those of similar ions, and that it would be desirable (as soon as sufficient plutonium became available) to determine the solubilities of such compounds as the oxalate, phosphate, fluoride, iodate, and peroxide. Such data were needed to confirm deductions based on the tracer experiments.

We conceived the principle of the oxidation-reduction cycle, as applied to the separations processes that were to become so useful later. This principle applied to any process involving the use of a substance which carried plutonium in one of its oxidation states but not in another. By use of this principle, for example, a carrier could be used to carry plutonium in one oxidation state and thus to separate it from uranium and the fission products. Then the carrier and the plutonium could be dissolved, the oxidation state of the plutonium changed, and the carrier reprecipitated, leaving the plutonium in solution. The oxidation state of the plutonium could again be changed and the cycles repeated. With this type of procedure, only a contaminating element having a chemistry nearly identical with the plutonium itself would fail to separate if a large number of oxidation-reduction cycles were employed. This principle, of course, applies to other types of processes, such as solvent extraction, adsorption, or volatility methods.

The plutonium isotope of major importance is the one with mass number 239. The search for this isotope, as a decay product of Np^{239}, was being conducted by the same group, with the collaboration of E. Segrè, simultaneously with the experiments leading to the discovery of plutonium. The isotope Pu^{239} was identified, and its possibilities as a nuclear energy source were established during the spring of 1941, using a sample prepared by the decay of Np^{239} pro-

duced by neutrons from the 60-inch cyclotron and later purified by taking advantage of the then-known chemistry of plutonium.

A sample of uranyl nitrate weighing 1.2 kilograms was distributed in a large paraffin block placed directly behind the beryllium target of the 60-inch cyclotron and was bombarded for two days with neutrons produced by the full deuteron beam. This uranyl nitrate was placed in a continuously operating glass extraction apparatus, in a room in the Chemistry Annex or "Rat House," and the uranyl nitrate was extracted into diethyl ether. The Np^{239} was isolated by use of the oxidation-reduction principle with lanthanum and cerium fluoride carrier and reprecipitated six times in order to remove all uranium impurity. For each of the numerous centrifugation procedures it was necessary to carry the material in a heavy lead shield from the chemistry building to Crocker Laboratory, which contained the only centrifuge available for this work. Measurement of the radiation from the Np^{239} made it possible to calculate that 0.5 microgram was present to yield Pu^{239} upon decay. (The resulting alpha activity corresponded to a half life of 30,000 years for the daughter Pu^{239}.)

Using neutrons produced by the 37-inch cyclotron in the University of California Old Radiation Laboratory, the group first demonstrated on March 28, 1941, with the sample containing 0.5 microgram of Pu^{239}, that this isotope undergoes slow neutron-induced fission with a cross section even larger than that of U^{235}. The sample was placed near the screened window of an ionization chamber, which was imbedded in paraffin near the beryllium target of the 37-inch cyclotron. This gave a small but detectable fission rate when a six-microampere beam of deuterons was used. In order to increase the accuracy of the measurement of the fission cross section, this sample, which had about five milligrams of rare-earth carrier material, was subjected to an oxidation-reduction chemical procedure that reduced the amount of carrier to a few tenths of a milligram. A fission cross section for Pu^{239} some 50 per cent greater than that for U^{235} was found, in remarkable agreement with the accurate values which were determined later. A report of this work was registered on May 29, 1941, for publication in the *Physical Review*, but again the information was voluntarily withheld from actual publication until after the end of the war in 1946. This

demonstration that Pu^{239} undergoes fission with thermal neutrons with a large probability, showing that all the neutrons emitted in the process are eligible to cause further fissions, established the great value of this isotope, and the recognition of this by E. O. Lawrence and others led to the wartime Plutonium Project for its production on a large scale, looking toward its possible use in a nuclear weapon.

1.3 The Metallurgical Project

1.3a The Production Problem

L. A. Turner was apparently the first to conceive the outline of the procedure which would be used for the large-scale production of plutonium. In order to understand the production problem, let us summarize the reactions of the two isotopes of uranium with neutrons:

(1) $U^{235} + n \rightarrow$ fission products + neutrons + energy

(2) $U^{238} + n \rightarrow U^{239} \rightarrow Np^{239} \rightarrow Pu^{239}$.

One of the questions which posed itself immediately was the following: Is it possible by use of the mixture of the uranium isotopes as it occurs in natural uranium, consisting of about 0.7 per cent of U^{235} and 99.3 per cent of U^{238} by weight, to cause a chain reaction to occur on a very large scale? If so, the extra neutrons produced in the fission of U^{235} would be absorbed by U^{238} to form the desired isotope, Pu^{239}, in large quantity.

The other question which of necessity came up for immediate discussion was: Would it be possible to devise, in a reasonable period of time, chemical means for separating this Pu^{239} from the uranium and from the tremendous fission-product radioactivities due to the many fission-product elements that would be present with it?

These were the two staggering problems which formed the basis of the Plutonium Project. Their solutions were to a large extent unrelated, and the development program in connection with each of these problems was, of course, in the hands of research men in different fields, physics and chemistry.

It is beyond the scope of the present discussion to give more than a brief description of the development of the chain-reacting

units called "piles" for the production of plutonium. The ideas for this originated with E. Fermi and co-workers at Columbia, and E. P. Wigner and associates at Princeton University. Fermi and L. Szilard were the first to recognize that the proper balance in the absorption of the secondary-fission neutrons could be obtained in a heterogeneous lattice arrangement of solid pieces of uranium distributed in a more or less regular pattern throughout a graphite base. The graphite serves to slow down the fast neutrons produced in the fission reaction without absorbing them appreciably, and the two reactions listed above take place predominantly with the slowed neutrons. The original graphite-uranium pile, which became the basis for the production unit, was the result of the famous initial pioneering work of Fermi, H. L. Anderson, W. H. Zinn, B. T. Feld, G. Weil, and their associates carried on at the University of Chicago, where such work had also been carried on by S. K. Allison, H. W. Newson, and co-workers. The first successful operation of the chain reaction, opening the atomic age, took place on December 2, 1942, under the West Stands at the Stagg Stadium football field at the University of Chicago. This reactor was soon moved out to a specially constructed building at Argonne Forest, then known as "Site A," where further important tests were carried on. It was not planned as a source of plutonium.

The early work of the chemistry group at the University of California formed the basis for the later development of the process used in the separation of plutonium from uranium and fission products in the large manufacturing plants. This process was based upon the use of the two oxidation states of plutonium, and a great deal of our earliest work was concerned with the study of these states on the tracer scale.

1.3b The Metallurgical Laboratory and Project

Early in 1942, following a high-level decision made in Washington, D.C., on December 6, 1941, physicists who had been working on the development of the chain reaction and chemists who had been working on the development of separation processes for the plutonium assembled at the Metallurgical Laboratory of the University of Chicago. In time, other scientists—chemists, physicists, engineers, biologists, and medical men—assembled here, to solve

problems related to those described above. Although the Metallurgical Laboratory (the forerunner of the present Argonne National Laboratory) was the center of the activity, there were more than seventy research groups in various parts of the country that participated in the "Metallurgical Project" (a code name for the "Plutonium Project"). This entire Project was under the able direction of A. H. Compton. About five thousand persons were engaged at the peak, of whom about two thousand were at the Metallurgical Laboratory in Chicago. N. Hilberry was Assistant, or Associate, Director of the Project throughout most of its history. Allison also served as Associate Project Director during part of the early period. R. L. Doan, and later Allison followed by F. Daniels, served as the Director of the Metallurgical Laboratory, while J. C. Stearns, R. S. Mulliken, and Z. Jeffries gave valuable administrative and advisory help.

Groups of physicists devoted to finding the best conditions for the production of the uranium chain reaction were headed by Fermi, Allison, and M. D. Whitaker. Wigner, G. Young, J. A. Wheeler, and others made important contributions to the design of the production reactors, which, on the basis of their early ideas, were soon visualized and finally built as water-cooled, aluminum-sheathed, uranium slugs embedded in a very pure graphite moderator. Szilard helped in all phases of the problem. Although it is beyond the scope of the present account to describe the work on the physics, engineering, and other aspects of the plutonium-production problem, it should be mentioned that important contributions were made by L. B. Borst, G. Breit, J. C. Chipman, E. C. Creutz, A. J. Dempster, A. B. Greninger, J. P. Howe, D. J. Hughes, M. C. Leverett, J. H. Manley, J. Marshall, L. Marshall, T. V. Moore, H. W. Newson, H. D. Smyth, A. H. Snell, E. S. Steinbach, E. Teller, H. C. Vernon, W. W. Watson, A. Wattenberg, G. Weil, A. M. Weinberg, and V. C. Wilson. H. N. McCoy helped in the organization of the Chemistry Division. R. S. Stone, with the help of S. T. Cantril, had supervision over the problem of radiation protection, and they were aided at the various sites by K. S. Cole, G. Failla, J. G. Hamilton, L. O. Jacobson, H. M. Parker, E. O. Wollan, and others. The important problem of the reduction of the uranium to very pure uranium metal

was solved satisfactorily in an amazingly short time by F. H. Spedding and his associates, I. B. Johns, Jr., W. H. Keller, and H. A. Wilhelm, all at Iowa State College, and also by C. J. Rodden and his co-workers at the National Bureau of Standards, with the production of important smaller amounts by J. W. Marden and associates of the Westinghouse Company. J. R. Ruhoff and the Mallinckrodt Chemical Works are to be credited with the production of the pure uranium salts needed as a starting point for the production of the metal in quantity. The procurement of sufficient quantities of pure graphite, a very difficult problem, was solved through the efforts of Hilberry, Doan, and others; the quantities of high purity material needed for the first reactor at Chicago were furnished by the Speer Carbon Company and the National Carbon Company.

The Metallurgical Project was initially the responsibility of a committee headed by J. B. Conant and L. J. Briggs as a part of V. Bush's wartime Office of Scientific Research and Development. The Project became a part of the U. S. Army Manhattan Engineer District, known as the "Manhattan District," in September 1942. As is well known, the Manhattan District, which also took on similar responsibility with respect to the production and use of U^{235}, was operated under the over-all direction of General Leslie R. Groves, with the able assistance of Colonel K. D. Nichols, until after the end of the war, when the Atomic Energy Commission took over. Major A. V. Peterson had special responsibility with respect to the Metallurgical Laboratory.

The duPont Company agreed late in 1942 to take on the responsibility for the building and operation of the plutonium-production plant, which would be built, it was finally decided, at Hanford, Washington. From somewhat before this time until the successful completion of the job, hundreds of duPont scientists and engineers became a part of the Project. Initial negotiations with duPont involved C. M. A. Stine, E. K. Bolton, T. C. Gary, and R. Williams of that company. Much of the top direction of the duPont effort was centered in Williams and in C. H. Greenewalt for the technical side of the job, in R. M. Evans for production, and in G. M. Read for design and construction. Leaders in the technical side of the effort included G. D. Graves, B. H. Mackey,

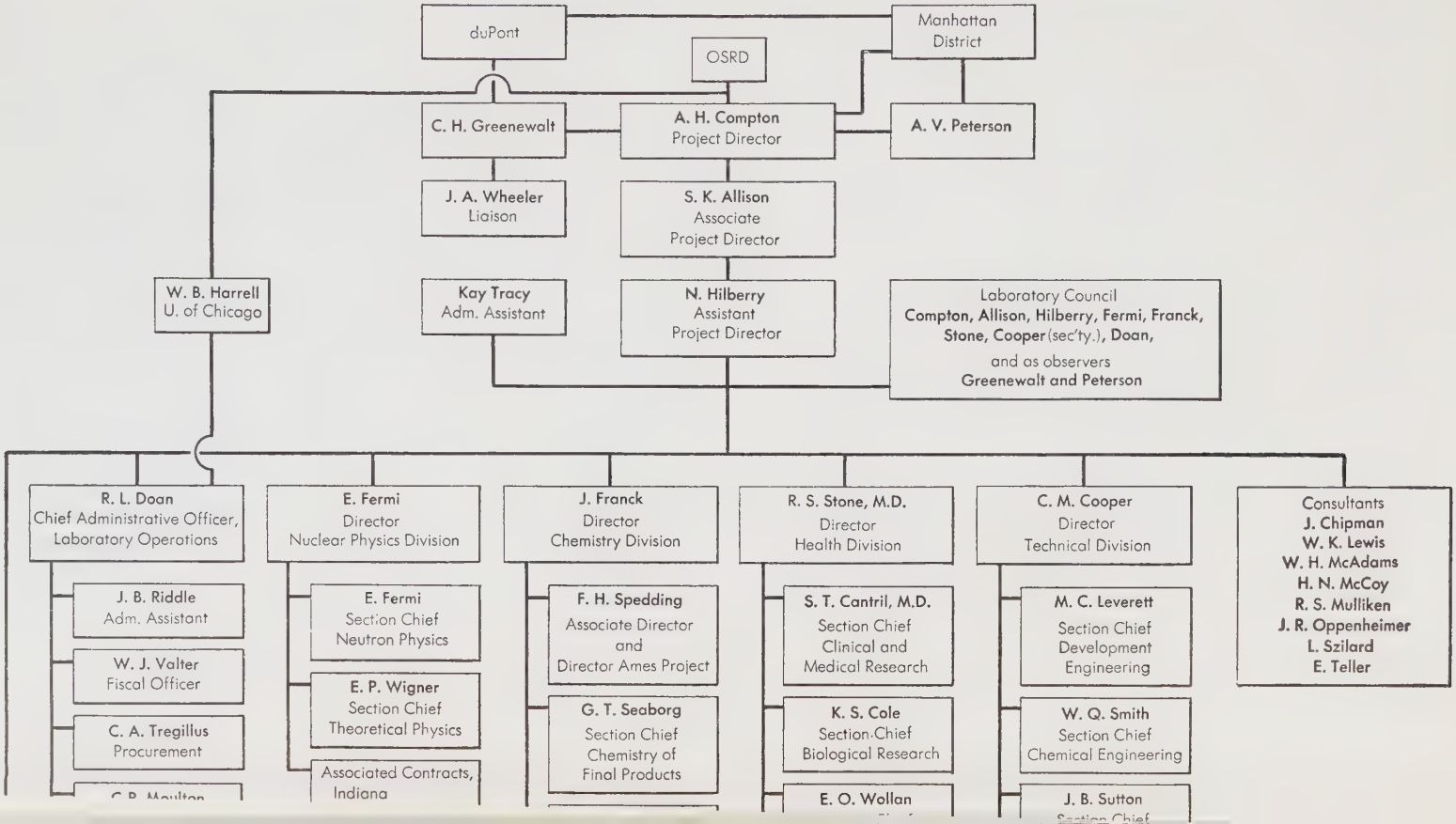
J. N. Tilley, L. Squires, J. E. Cole, H. Worthington, W. E. Kirst, and J. B. Miles.

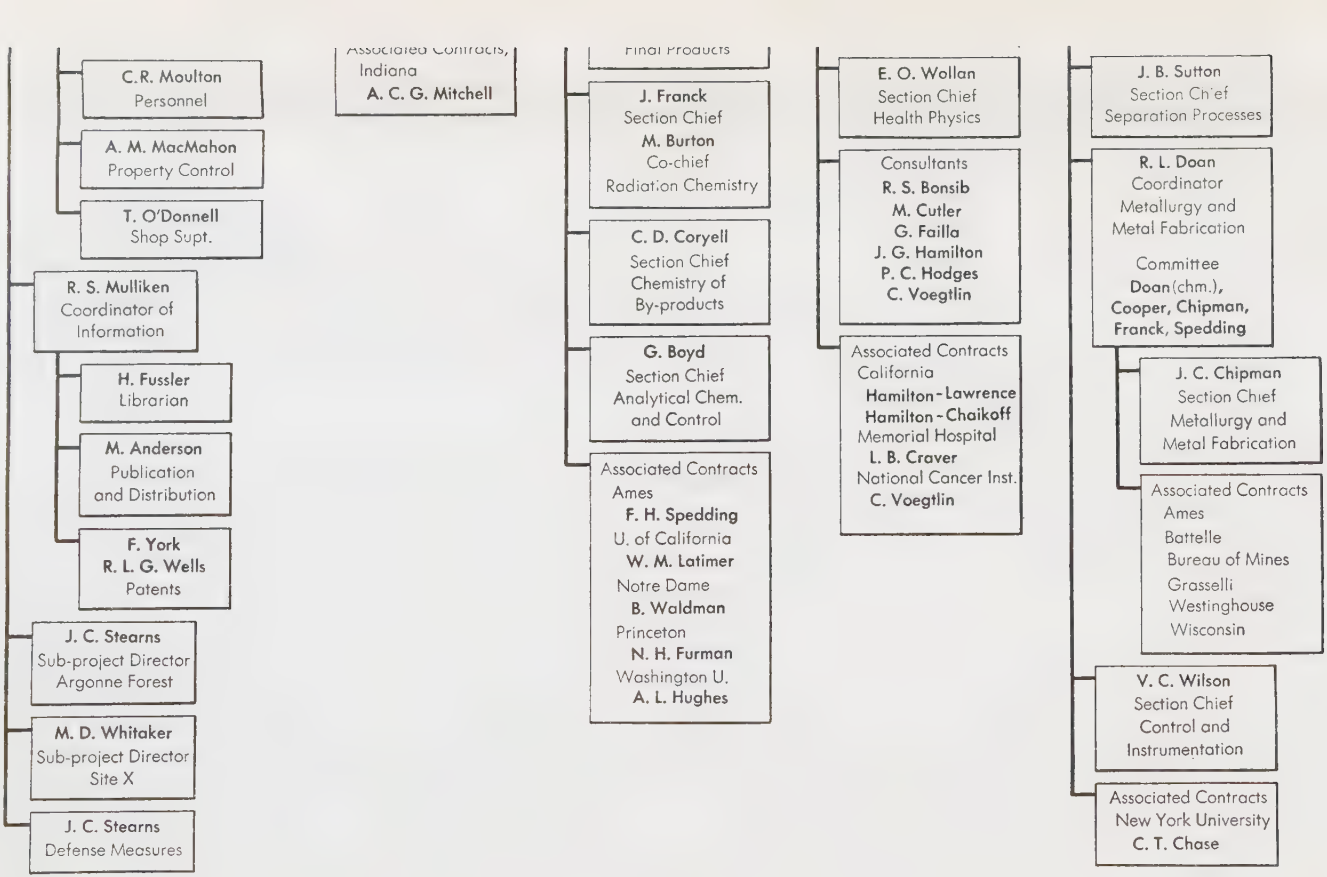
Thus it can be seen that the organization of the Metallurgical Project and the Metallurgical Laboratory and the associated efforts at other sites was a complex matter. Much of the discussion which follows will serve to illustrate the interrelationships between the various sites. Although the organization changed with time, the chart shown in Table 1.1, dated January 23, 1943, is good for illustrative purposes because it lists the key administrative people based at Chicago at a time when the Project was in full swing and before the departure of a number of these to other sites.

1.3c The Chemical Extraction Problem

The responsibility for devising the chemical means for separating the Pu^{239} from the uranium and fission products, as well as solving numerous other chemical problems related to obtaining a successful chain reactor for the production of the Pu^{239}, rested with the Chemistry Division of the Metallurgical Laboratory. This division was successively under the direction of F. H. Spedding, S. K. Allison, J. Franck, T. R. Hogness, and F. Daniels. W. C. Johnson or P. W. Selwood served as associate director and L. B. Arnold, Jr., as assistant director during part of the time. The members of the division occupied temporary quarters in Jones and Kent Chemical Laboratories of the University of Chicago during 1942. The group which I directed, with the assistance of I. Perlman, in the research on the plutonium-extraction process, occupied quarters which were extremely limited in size (one large and several small rooms at one end of the fourth floor of Jones Laboratory). In December of 1942, the group working on the plutonium-extraction process and related problems, and the groups working on the fission products (under the leadership of C. D. Coryell), effects of radiation on critical materials and processes (under M. B. Burton), and analytical and other problems (under G. E. Boyd) moved to new quarters, the "New Chemistry" building on the edge of the campus. However, the space situation was soon critical again and an addition to this building, the "Chemistry Annex" or "New New Chemistry" building was added late in 1943. (These buildings on Ingleside Avenue were torn down a few years after the end of the war.)

Table 1.1 Organization Chart of the Metallurgical Project and Metallurgical Laboratory (as of January 23, 1943)




C.R. Moulton
Personnel
A. M. MacMahon
Property Control
T. O'Donnell
Shop Supt.
R. S. Mulliken
Coordinator of Information
H. Fussler
Librarian
M. Anderson
Publication and Distribution
F. York
R. L. G. Wells
Patents
J. C. Stearns
Sub-project Director
Argonne Forest
M. D. Whitaker
Sub-project Director
Site X
J. C. Stearns
Defense Measures
Associated Contracts,
Indiana
A. C. G. Mitchell
Final Products
J. Franck
Section Chief
M. Burton
Co-chief
Radiation Chemistry
C. D. Coryell
Section Chief
Chemistry of By-products
G. Boyd
Section Chief
Analytical Chem. and Control
Associated Contracts
Ames
F. H. Spedding
U. of California
W. M. Latimer
Notre Dame
B. Waldman
Princeton
N. H. Furman
Washington U.
A. L. Hughes
E. O. Wollan
Section Chief
Health Physics
Consultants
R. S. Bonsib
M. Cutler
G. Failla
J. G. Hamilton
P. C. Hodges
C. Voegtlin
Associated Contracts
California
Hamilton-Lawrence
Hamilton-Chaikoff
Memorial Hospital
L. B. Craver
National Cancer Inst.
C. Voegtlin
J. B. Sutton
Section Chief
Separation Processes
R. L. Doan
Coordinator
Metallurgy and Metal Fabrication
Committee
Doan (chm.),
Cooper, Chipman,
Franck, Spedding
J. C. Chipman
Section Chief
Metallurgy and Metal Fabrication
Associated Contracts
Ames
Battelle
Bureau of Mines
Grasselli
Westinghouse
Wisconsin
V. C. Wilson
Section Chief
Control and Instrumentation
Associated Contracts
New York University
C. T. Chase

It should be added that the problem of assembling the large number of chemists and chemical engineers that were eventually needed at the Metallurgical Laboratory, many of whom went to the Clinton Laboratories or to Hanford, was a very challenging one. Facility with the methods of radiochemistry was needed in most instances, and the available supply of trained radiochemists was essentially nil. Thus we found it necessary to train scientists by the hundreds in the fundamentals and the techniques of this discipline. In order to build up my own staff, for example, I called on most of the competent scientists in my acquaintanceship to join us and these in turn called on their friends. Thus our group eventually included a large fraction of my fellow chemistry students who had attended the University of California at Los Angeles as my classmates, in addition to many of my colleagues from the University of California at Berkeley. I gave a lecture course in nuclear chemistry during the summer of 1942, and the notes covering this course, taken by C. D. Coryell, were reprinted by the thousands.

During the first months at the Metallurgical Laboratory, intensive effort was directed toward defining the chemical-separation process to be used in the production plants which were then being planned. Among the possible procedures that were investigated were precipitation, solvent-extraction, volatility, adsorption-elution, and pyrometallurgical and pyrochemical processes; in fact, all of the types of processes now in use or under investigation were included in this early scouting program of the year 1942. The solvent-extraction approach was investigated by D. E. Koshland, Jr., the volatility approach by H. S. Brown and O. F. Hill and later E. G. Bohlmann, pyrochemical and pyrometallurgical procedures by T. T. Magel and M. Cefola, and the adsorption-elution method by J. E. Willard and E. H. Turk as well as Boyd, A. W. Adamson, E. E. Motta, E. R. Russell, J. Schubert, and their co-workers. However, it was decided before the end of 1942 to use a precipitation process because this seemed to offer the greatest certainty of at least limited success in the short time interval involved, even though it did not seem to offer the greatest ultimate efficiency and would not lead to the recovery of the uranium for reuse.

The problem of separating the new element plutonium from

uranium and fission products might not at first seem difficult, for it was, indeed, primarily a chemical problem. However, it differed in a great many ways from ordinary chemical problems, and these differences made the solution of the problem as a whole much more difficult, even though some of the differences actually helped the solution. From the beginning, our limited time seemed the most nearly insurmountable difficulty. It was by no means possible to complete the design and testing of the process before it had to be placed in operation. Even a simple chemical process usually requires a much longer time to place in large-scale operation than did the plutonium-separation process, even though the latter cannot be regarded as either simple or short.

The problem which had to be met during the fall of 1942 was that of developing a separation process which would meet the demanding requirements. The process had to accomplish a separation of plutonium in high yield and purity from many tons of uranium in which the plutonium was present at a maximum concentration of about 250 parts per million. Because of this low concentration, compounds of plutonium could not be precipitated, and any precipitation-separation process had to be based upon coprecipitation phenomena, i.e. the use of so-called "carriers" for plutonium. At the same time, the radioactive fission products produced along with plutonium in the uranium (as a result of the fission of U^{235}) had to be separated so that less than one part in 10^7 parts originally present with the plutonium would exist with the final product from the process. This requirement was necessary in order to make it safe to handle the plutonium, for without a separation of the fission products, the plutonium from each ton of uranium would have more than 10^5 curies of energetic gamma radiation associated with it. The process of separating fission products was called "decontamination." Thus a unique feature of the process was the necessity of separating a wide variety of elements completely from the final product and of accomplishing these separations by remote control behind large amounts of shielding in order to protect operating personnel from the hazards of the radiation. The finally decontaminated plutonium compound that was to be provided to those responsible for its ultimate use had to be one that would facilitate those final steps; it had to be a compound or solution of small bulk

that could be shipped without difficulty, and it had to be of a composition that could be easily subjected to further purification. The separation process had to meet the further requirement that a "critical mass" of plutonium, which would lead to a disruptive nuclear chain reaction, should not accumulate at any step of the procedure.

If large amounts of plutonium had been available in the fall of 1942 and if its chemistry had been as well known as the chemistry of the more familiar elements, the task of developing the chemical process would still have been a formidable undertaking. Essentially all that was known about plutonium at this time was based upon secondary evidence from tracer experiments involving the infinitesimal amounts of the element which had been produced entirely by cyclotron bombardments. All of the plutonium (in the form of the isotopes Pu^{238} and Pu^{239}) used in the experiments up until the time of the operation of the Clinton reactor, with the exception of an experimental test of the separation process on the semiworks scale using some uranium oxide from the reactor at Argonne Forest, was cyclotron produced, using the cyclotrons at the University of California and Washington University. Tracer chemistry itself was a relatively new science; many of its phenomena were not clearly understood; and deductions based on it were often subject to doubt, particularly when applied to a new element. Added to the difficulty of devising the chemical process was the fact that only a few of the fission products had been identified, and many of these proved to be among the least well known of the chemical elements.

Operation of a chemical process by remote control behind massive shielding in an area which would become so highly radioactive after use that operating and maintenance personnel would not be able to enter the area for even brief periods of time to adjust and service equipment, made it imperative that the process be thoroughly tested in advance in the type of equipment to be used in the plant, in order to minimize the possibility of errors in the design of the process or the equipment. Furthermore, operational errors had to be kept to a minimum, and careful chemical control of the operations had to be maintained. In all of these considerations it was obviously desirable that the process to be operated be as short and as simple as possible. Similarly, the process from the standpoint of plant design should consist of a number of similar steps requiring

the same sort of equipment rather than consisting of steps which were so fundamentally different as to require many different types of equipment. At the same time, it seemed advisable to design the process and the equipment in such a way as to facilitate changes in case of failure. All of these requirements were met; in fact, the process was operated more successfully than even the most optimistic dared to hope and from the beginning gave high yields and decontamination factors.

Although it was felt that such a separation process would depend on the use of the two oxidation states of plutonium, which had been discovered during the early work at the University of California, the actual details, such as the best carrier compounds and best oxidizing and reducing agents, had not yet been discovered. S. G. Thompson is largely responsible for the conception and early development of the process which was finally chosen. The key to the process is the quantitative carrying of plutonium (IV) from acid solution by bismuth phosphate, an unexpected phenomenon which was discovered in December 1942, and the expected noncarrying of plutonium (VI) by the same carrier material. This method, known as the Bismuth Phosphate Process, operates as follows: Neutron-irradiated uranium is dissolved in nitric acid, and, after the addition of sulfuric acid to prevent the precipitation of uranium, plutonium (IV) is coprecipitated with bismuth phosphate. The precipitate is dissolved in nitric acid, the plutonium (IV) is oxidized to plutonium (VI), and a by-product precipitate of bismuth phosphate is formed and removed, the plutonium (VI) remaining in solution. After the reduction of plutonium (VI) to plutonium (IV), the latter is again coprecipitated with bismuth phosphate, and the whole "decontamination cycle" is repeated. At this point the carrier is changed to lanthanum fluoride, and a similar "oxidation-reduction cycle" is performed, using this carrier, thereby achieving further decontamination and concentration. The plutonium at this point is sufficiently concentrated that final purification can be accomplished without the use of carrier compounds and plutonium peroxide is precipitated from acid solution.

The following section is devoted to a detailed account of the evolution and development of the Bismuth Phosphate Process.

1.4 Evolution of the Bismuth Phosphate Process

Because of the large number of workers who contributed to the development of the Bismuth Phosphate Separation Process over a relatively short period of time, it is difficult, if not impossible, to place in proper perspective all of the significant contributions. Similarly, efforts to give due credit to all who contributed to this work must involve many errors of omission. Since the conditions surrounding the developmental work were so abnormal, no one person could maintain intimate contact with all of the experimental details or be fully aware of all of the important decisions leading to the final successful operation of the process. This, therefore, is an attempt to delineate the chronological development of its major features.

One of the most remarkable features of the Process is the limited time in which it was developed. The element plutonium was discovered in December 1940, and the first compound was isolated in August 1942, as will be described. The unusual properties of bismuth phosphate as a carrier for plutonium were discovered in December 1942, and the Bismuth Phosphate Separation Process was placed in successful operation in the pilot plant at Clinton Laboratories in Tennessee in December 1943. Thus in actually less than one year the process development work was almost completed before the total quantity of plutonium available from cyclotron bombardments had reached two milligrams. Additional developmental work preceded the beginning of operation of the vast processing plants at Hanford, Washington, in December 1944. Finally, it is significant that only four and one-half years elapsed between the discovery of plutonium and its first use as a source of nuclear energy for military purposes. Accomplishment of this objective during World War II required not only tremendous financial resources, engineering and chemical skill, careful planning and organization, high priorities for material, skilled manpower, and construction facilities, but also imagination and (perhaps as much as anything else) a considerable measure of good fortune.

As a result of early work at Berkeley, one separation process had

evolved already, based on the oxidation and reduction of plutonium and its nonprecipitation and precipitation with a lanthanum fluoride carrier. This was called the "Lanthanum Fluoride Process," and it later became an integral part of the Bismuth Phosphate Process. Although the Lanthanum Fluoride Process seemed to be sound chemically, there were many potential difficulties inherent in its operation in the plant. In October 1942, the process was tentatively, albeit reluctantly, accepted as the best available prospect for use in the production plants which were to be constructed later, the design of which was already under consideration.

The early development of the Lanthanum Fluoride Process pointed out the necessity of identifying the major fission products so that the chemistry of these elements could be taken into account in working out the separation processes. Therefore, a brief survey of these fission products—their yields, half lives, and other radiation characteristics—was made during August and September 1942, by B. Goldschmidt, a visitor from France, and I. Perlman. The results of these investigations were extremely useful. More complete information on the fission products became available later as a result of the work of C. D. Coryell and his group. The results of this work, all of which were published under the names of the individual investigators, after the war, in the Plutonium Project Record and elsewhere, were of considerable practical value in perfecting and testing the process later.

In October 1942 the chemists at Chicago who were working on the chemistry of plutonium and attempting to develop the chemical process numbered about twenty men, but the number began to increase at about that time. The over-all direction of the Metallurgical Laboratory research on the separation process for plutonium was my responsibility. The investigation of various phases of the task was directed by Perlman, S. G. Thompson, J. E. Willard, G. W. Watt, and F. W. Albaugh, with groups led by J. L. Dreher, R. C. Thompson, D. G. Pye, and J. R. Gilbreath. (Numerous other contributors at this Laboratory and at other sites will be mentioned in later parts of this section and in later sections.)

Separate groups of chemists were responsible for the identification and characterization of the fission products, for analytical problems, and for the study of the effects of radiation on the chemical

extraction process and on critical materials. The fission-product research was the responsibility of Coryell, with the help of N. Sugarman, A. Turkevich, W. Rubinson, E. P. Steinberg, L. Winsberg, S. Katcoff, N. Elliott, H. A. Levy, D. N. Hume, E. L. Brady, R. R. Edwards, L. E. Glendenin, H. L. Finston, D. W. Engelkemeir, J. A. Swartout, N. E. Ballou, M. S. Freedman, R. P. Schuman, T. B. Novey, C. R. Dillard, W. H. Burgus, T. H. Davies, J. A. Marinsky, R. P. Metcalf, J. A. Seiler, and co-workers. G. E. Boyd, in charge of the analytical chemistry program, had the help of H. A. Potratz, M. S. Fred, R. E. Curtis, J. Schubert, and others, while M. B. Burton, leader of the research on the effects of radiation, was assisted by A. O. Allen, T. J. Neubert, W. M. Garrison, A. Novick, E. Shapiro, C. V. Cannon, and others. By the summer of 1943 the chemistry division including these separate groups consisted of several hundred people and the project was expanding rapidly, although the chemists actually working on the separation process which was finally adopted numbered less than twenty-five, excluding duPont personnel. Sugarman replaced Coryell as leader of the remaining fission-product research group, when the latter moved a large part of the group with him to Clinton Laboratories. Similarly, E. B. Ashcraft and D. S. McKinney took over the responsibility for the analytical chemistry program when Boyd took over the leadership of this work at Clinton Laboratories.

The early chemical investigations had indicated the existence of plutonium in aqueous solution as a quadrivalent ion. By analogy with uranium (IV), thorium (IV), and other quadrivalent ions, it was considered likely that plutonium (IV) would form a phosphate that would be insoluble in solutions of moderate acidity. Furthermore, it would be expected to have a pronounced tendency to coprecipitate with these analogous compounds. During October, November, and December 1942 the phosphates known to be insoluble in acid solutions were investigated as carriers for plutonium by S. G. Thompson. Zirconium phosphate gave promising results at first and supported microchemical measurements which showed that plutonium (IV) phosphate had a low solubility. Zirconium phosphate, however, under the conditions tested did not carry plutonium completely and consistently at the higher concentrations of plutonium to be expected in a process to be operated at Han-

ford. Others of the more insoluble phosphates were tried, including thorium (IV), uranium (IV), titanium (IV), cerium (IV), and niobium (V) phosphates. Because of the highly gelatinous nature of these compounds, their failure to carry plutonium, or other undesirable features, they were excluded from further consideration as carriers.

The use of zirconium phosphate as a carrier, although unsatisfactory in itself, did point out the value of a process involving the use of a phosphate carrier. There was reluctance to abandon this approach, despite the fact that the list of insoluble phosphates was very limited. In any consideration of the phosphates as specific carriers for the separation of plutonium from uranium and fission products, it was necessary that not more than a small proportion of the uranium (which was necessarily present at high concentrations) be allowed to precipitate as the bulky uranium phosphate. In order to prevent such precipitation of uranium (VI) phosphate it was necessary to maintain high acidities. At such high acid concentrations there are very few elements which are precipitated by the addition of phosphoric acid. Those mentioned in the preceding paragraph were, of course, exceptions. Another possibility seemed to be bismuth phosphate, although knowledge of the principles of coprecipitation at the time seemed to preclude any probability that this phosphate would carry the plutonium supposedly of oxidation state IV.

In early December 1942 the first tests of bismuth phosphate as a carrier for plutonium were made, but these tests were unsatisfactory. The compound appeared to be too soluble at the high acidities necessary to prevent the precipitation of uranium phosphate. This failure was due to a practice that had become established in the study of fluoride and other carriers, i.e. the precipitation of only very small amounts of carrier.

On December 19, 1942, S. G. Thompson, who was probably the first to recognize the possibilities and advantages of a phosphate process, attempted the precipitation of a relatively large concentration of bismuth (III) as bismuth phosphate. Upon digestion of the uranyl nitrate solutions containing bismuth (III) and phosphoric acid at elevated temperatures, precipitation occurred slowly but fairly completely when the time of digestion was extended.

Surprisingly enough, the precipitate carried more than 98 per cent of the plutonium, and frequent repetition led to the conclusion that bismuth phosphate presented attractive possibilities as a carrier in a separations process.

On the basis of these tracer experiments alone it was not possible to conclude that bismuth phosphate would carry plutonium at the high concentrations expected to prevail in the large-scale separations plant being planned for operation at Hanford. However, the first ultramicroscale experiments performed very soon thereafter by B. B. Cunningham, using methods described below, showed that bismuth phosphate was capable of carrying plutonium at concentrations up to and above those anticipated for actual plant operations.

In a precipitation process the carrier must possess, in addition to its high capacity to carry, other characteristics which render it useful in practice. Such properties as density, ease of separation from solution by centrifugation or filtration, and solubilities in media for subsequent processing are of great importance in the operation of the separations process. Bismuth phosphate possessed these desirable characteristics in a remarkable degree. In fact, it was largely because the precipitates were filterable and the solutions involved had tolerable corrosion properties that the method was considered at all promising at the start. Later it was decided to use centrifuges in the separations plant, and the precipitates were also remarkably well adapted to this mode of separation. In addition, bismuth phosphate was relatively soluble in more concentrated nitric acid and could be reprecipitated merely by dilution. Its extremely high solubility in hydrochloric acid was convenient in laboratory work.

Following the discovery that bismuth phosphate is a useful carrier for plutonium, the early months of 1943 were spent in working out the basic conditions under which the new carrier could be used in a process. This work included an extensive investigation of the variables involved in the extraction of plutonium from a solution of uranium and fission products as well as the broad outline of oxidation-reduction cycles in which bismuth phosphate was precipitated consecutively with plutonium alternately in its oxidized (VI) and reduced (IV) states. This work showed that bismuth

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phosphate did not carry the highest oxidation state (VI) of plutonium. It was also found that bismuth phosphate is a very specific carrier for the separation of plutonium from fission products.

Reprecipitation of bismuth phosphate, however, did not continue to remove fission-product activities as rapidly as did the first step, since certain phosphate-insoluble fission products (e.g. zirconium and niobium) were carried moderately well by the precipitates, particularly in the absence of uranium. It was obvious, therefore, that the oxidation-reduction-cycle principle had to be employed, if the process was to provide adequate decontamination. Other possibilities, of course, involved coupling of the bismuth phosphate and other procedures. Such possibilities were investigated with varying degrees of intensity during the next two years. Although the final process chosen was, in fact, a combination of the bismuth phosphate and lanthanum fluoride procedures, the latter was selected primarily to provide for concentration of the plutonium rather than to achieve additional decontamination.

The laboratory work which followed during 1943 and 1944 was largely devoted to the selection of oxidizing and reducing agents for the process, in working out optimum conditions for each step, the improvement of decontamination, and in developing procedures for the concentration and isolation of plutonium. More will be said later about the concentration and isolation procedures; they were regarded as relatively minor problems in early 1943.

During this period of early development of the Bismuth Phosphate Process, little attention was given to the new process by the chemical engineers, although they kept informed as to the progress of its development, because the decision had been made to develop equipment for a precipitation process adaptable to any similar system. Meanwhile, they had constructed a semi-works which was simply a small-scale pilot plant composed of the same general type of equipment as was planned for use in a large plant later. The purpose of the semi-works was to test a process, especially the mechanical steps, under as nearly as possible the same conditions as would be expected to prevail in a large-scale plant. In this way many difficulties with the process could be detected in time to make corrections in either the equipment or the chemical steps before building the plant and starting operation. The design and develop-

ment of the separations process semi-works at Chicago was done largely by a small group of men on loan from duPont. The original group of engineers, which arrived in August 1942, operated under the supervision of C. M. Cooper, and included R. S. Apple, L. C. Peery, P. S. Vincent, D. S. Webster, F. B. Vaughan, and also W. A. Rodger from the Parke-Davis Company. W. Q. Smith came a few months later to aid in the direction of this effort, along with M. D. Peterson and J. A. Lane, all from the duPont Company. All of these men worked closely with the chemists, often with them in the laboratories. Their contribution to the development of the process was considerable, particularly in relation to its adaptation to large-scale equipment and the suggestion of methods of practical improvement.

The original semi-works was designed for the Lanthanum Fluoride Process and for several months was concerned largely with the evaluation of this Process. Difficulties soon became apparent, particularly with respect to the corrosion of the stainless-steel equipment by fluoride solutions. It was found difficult to maintain plutonium in its highest oxidation state in solutions containing fluorides and to develop a satisfactory coupling step between oxidation-reduction cycles in which the lanthanum fluoride carrier had to be dissolved or converted to the acid-soluble hydroxide. These experiences provided a preview of the types of difficulties to be encountered later with the Bismuth Phosphate Process and were taken into account throughout the development and improvement of the latter.

In the early part of 1943 difficulties with the Lanthanum Fluoride Process led to increased interest in the use of bismuth phosphate carrier. Greater effort was directed toward its further development, and particular attention was given to the study of suitable oxidizing and reducing agents. A few preliminary tests were made in the semi-works, and the results were most promising.

It was not until early in 1943 that the role of the duPont company in the nuclear energy program became formalized. The project work was assigned to the Explosives Department in a new division known as TNX, and this assignment led to an expenditure of about $350,000,000 for the establishment of the largest plant ever constructed and operated by the duPont company up to that time.

Responsibility for the fundamental research and development essential to the success of the work done by duPont remained with the University of Chicago. DuPont was asked first to engineer, design, and construct a small pilot plant which was to be located near Clinton, Tennessee, but operated by the University. In addition, a large number of duPont technical men were loaned to the University, which needed the skilled assistance provided by industrial experience.

As a result, duPont began to have a major influence, beginning in February and March 1943, upon the development of the separations process. They began to evaluate the various possible processes which were being developed at that time. A group of process-development chemists from duPont was organized under the direction of J. B. Sutton at the Metallurgical Laboratory in January and February 1943, and included J. H. Balthis, Jr., C. M. Olson, J. H. Peterson, E. R. Gilbert, B. F. Faris, and G. W. Stahl. These men worked in an engineering division, which also carried other responsibilities and which, under Cooper, had already been in operation for a number of months. DuPont technical men soon became attracted to the Bismuth Phosphate Process and in March and April 1943 began to put a major part of their effort into its development. They accomplished a great deal in the improvement of the Process and in confirmation of the previous work of the process chemists working with my group, which up to this time had been so small that less than six chemists could be spared for this work. Also, until this time, the chemical engineering group, which had been giving the major part of its effort to testing the Lanthanum Fluoride Process, had not been able to expand sufficiently to put forth much effort on testing the Bismuth Phosphate Process.

By May 1943 it had become clear that further concentration of effort was necessary to prepare the process for operation in the pilot plant at Clinton. DuPont personnel were particularly anxious that a single process be chosen, and a date was set for a meeting at which the decision would be made. On June 1, 1943, this meeting, attended by representatives of the duPont Company and the Metallurgical Laboratory, together with the chemists and engineers who had been most closely associated with the development of chemical processes, was held in Chicago. All available information

relative to the Bismuth Phosphate and Lanthanum Fluoride Processes was summarized. The decision which had to be made was not an easy one. Even in the light of all of the available data there remained uncertainties, for example, with regard to corrosion problems associated with the Lanthanum Fluoride Process and to possible failure of complete coprecipitation of plutonium with bismuth phosphate at high concentrations of plutonium. In fact, it was not even certain that precipitation processes would necessarily prove superior to methods based upon solvent extraction, adsorption, or other phenomena. The decision in favor of the Bismuth Phosphate Process was largely influenced by my prediction of at least a 50 per cent yield and by C. H. Greenewalt's expressed preference for a process that would minimize the possibility of early equipment failures even at the expense of decreased yields.

During the spring and summer of 1943, many experiments were performed with the purpose of defining more exactly the conditions for operating the process. During this period the work of the following men was particularly noteworthy: R. A. James, D. R. Miller, E. H. Turk, V. R. Cooper, J. L. Dreher, N. R. Davidson, D. E. Koshland, Jr., W. J. Knox, G. R. Leader, A. H. Angerman and D. M. Ritter. Many experiments were tried in practically every case before suitable conditions could be established for each particular step. Only a few of the successful results will be mentioned. One was the use of sulfuric acid to hold the uranium in solution, presumably by the formation of a complex ion involving uranium (VI) and sulfate ion, during the precipitation of bismuth phosphate in the first extraction step. Conditions for the dissolution of bismuth phosphate in nitric acid for the oxidation-reduction cycles were established. Oxidizing agents to convert plutonium to its hexapositive state in solutions of bismuth phosphate in nitric acid were investigated, with the result that by summer, two appeared to be satisfactory. These were the combination of cerium (IV) with dichromate, and sodium bismuthate; and the latter was adopted later. Conditions for the precipitation of bismuth phosphate in solutions containing plutonium (VI) (the non-carriable state) were studied, and this step, named the "by-product precipitation" step, was developed. The search for new reducing agents resulted in the application of ferrous ion for this purpose. Somewhat later it was

found that nitrite ion best served to put plutonium in the IV state for the extraction step, i.e. the first precipitation of bismuth phosphate from the uranium solution. A crystal form of bismuth phosphate, the β-form—which was very slowly soluble in acid—was discovered; this made it necessary to develop process conditions that would make certain the more soluble α-form of bismuth phosphate was precipitated in the plutonium-carrying steps.

The laboratory and semi-works tests had now proceeded to a point where, in the summer of 1943, the necessity for rapid development of methods for concentration and isolation of plutonium had become apparent. Such methods had been investigated in connection with the Lanthanum Fluoride Process, but practically no work had been done on this phase of the Bismuth Phosphate Process. In the laboratory, dissolution of bismuth phosphate in hydrochloric acid and the coprecipitation of plutonium with rare-earth-fluoride carrier had been extensively used and was remarkably satisfactory because of the high solubility of bismuth phosphate in hydrochloric acid. But hydrochloric acid was very corrosive to the stainless steel equipment planned for use in the process, and there appeared to be no simple method of avoiding this difficulty. It became necessary to choose some concentration method which could be used in the semi-works equipment. It was at this point that the two precipitation processes which had been developed in parallel and which were both under consideration for use in the large-scale plants (i.e. the Bismuth Phosphate and Lanthanum Fluoride Processes) were combined, following a suggestion of L. C. Peery. The fluoride steps were used for the concentration of plutonium to reduce the bulk of carrier following the several steps in which the bismuth phosphate procedure was used, and the later choice of an isolation procedure was to involve the precipitation of plutonium as the peroxide, a procedure proposed by I. Perlman for the Lanthanum Fluoride Process. The real value of the combination did not become evident until later, when it became clear that fission products not well separated by the phosphate steps were efficiently separated by the fluoride steps. Furthermore, the use of the fluoride procedure was a protection against failure of the phosphate procedure, since in an emergency the former could have performed the extraction and decontamination steps.

The final step in the over-all extraction and decontamination process was to be the isolation process, the precipitation of the plutonium in the form of a compound without the use of a carrier, after the concentration step. It was necessary to make a decision on the process for the isolation procedure before any of the many methods under investigation at the Metallurgical Laboratory and at Clinton had been perfected, in order that the design of the Hanford equipment might begin on time. I recall being requested by Squires to select a process, even though no single one had yet been developed; I made the suggestion that it should be the peroxide precipitation procedure. Thus a single path was chosen, and the chemists were faced with the necessity of making a process work by one means or another. The very successful research that led to the perfection of the plutonium peroxide isolation procedure was carried out under the very able direction of G. W. Watt and D. G. Pye.

1.5 The Clinton Plant

It was agreed as early as September 1942 to locate the plutonium pilot plant in Tennessee. The move to the Clinton Engineer Works, or Clinton Laboratories, named for the neighboring village of Clinton, took place during the fall of 1943. The plant had been largely built by that time and a nearby village, given the name of Oak Ridge, was constructed to house the personnel associated with the operation. M. D. Whitaker became the head of the plant; R. L. Doan, the director of research; W. C. Johnson, and later J. R. Coe, Jr., the head of the Chemistry Division; A. H. Snell, a leader of the Physics Division; M. C. Leverett, the head of the Technical Division; and K. Z. Morgan and J. E. Wirth, the heads of health physics and biology. Metallurgical Project Director Compton moved to the site to watch over the operations. L. B. Borst, L. W. Nordheim, and E. O. Wollan directed important segments of the work.

The Clinton Laboratories, also known by the code name of "Site X," was the responsibility of the University of Chicago, with personnel from the duPont Company playing the key role in the design, building, and operation of the air-cooled graphite reactor

and the bismuth phosphate extraction plant which served as prototypes or pilot plants for the later Hanford operation. (After the war the Clinton Laboratories became the Oak Ridge National Laboratory, operated first by the Monsanto Chemical Company, soon to be followed by the Union Carbide Company, the present operator.) S. W. Pratt managed these pilot production activities from the standpoint of the duPont Company, with the help of W. C. Kay and with L. K. Wyatt in charge of the reactor and F. B. Vaughan in charge of the chemical extraction plant.

During the period August through November 1943 most of the chemists and engineers associated with the work on chemical processes moved from the Metallurgical Laboratory to the Clinton Laboratories to prepare for the beginning of plant operations there. The chain-reacting pile that had been under construction since early in 1943 began to operate at low-power level on November 4, 1943. Its performance was excellent. Construction of the separations plant was nearing completion. The process semi-works had been transferred from Chicago and began to operate in September 1943 in a division under the direction of O. H. Greager. The group of process development chemists under J. B. Sutton transferred to the Clinton Laboratories in November. A large number of chemists transferred from the Metallurgical Laboratory and continued on process work under the direction of I. Perlman, with groups under the leadership of S. G. English, D. R. Miller, D. E. Koshland, Jr., V. R. Cooper, and B. A. Fries. Table 1.2 shows a summary of the organization and various groups that worked under Perlman at this time. R. W. Stoughton later headed a group working on U^{233}. Other groups with C. D. Coryell (on fission-product research, hot-laboratory operations, and process thermodynamics) and G. E. Boyd (on analytical chemistry and continued research on potential adsorption processes as possible alternate methods for the separation and decontamination of plutonium) were similarly transferred to Clinton, and these latter groups all worked in the chemistry division under W. C. Johnson. H. S. Brown, after initially directing research on volatility processes, served as assistant director of the Chemistry Division.

The first uranium from the pile entered the separations plant on December 20, 1943. By the end of January, 1944, metal from

TABLE 1.2 *Organization Chart for Section C-I, Clinton Laboratories (early 1944)*

I. Perlman—SECTION CHIEF
S. G. English—ASSOCIATE SECTION CHIEF
Mrs. D. C. Silverman—SECRETARY

Group 1—Process Research

D. R. Miller—GROUP LEADER
A. F. Clifford
A. H. Germany
J. Halperin
J. P. Hunt
G. L. Johnson
W. J. Knox
D. E. Koshland, Jr.
J. P. MacBride
E. D. Rose
R. B. Scott
C. Smith
Van Bueron
E. L. Zimmerman

Group 2—Process Service

S. G. English—GROUP LEADER
J. O. Blomeke
E. G. Bohlmann
O. F. Hill
O. E. Myers

Group 3—Physical Measurements

C. J. Borkowski—GROUP LEADER
R. L. Butenhoff
R. A. Dandl
J. K. East
O. Flateau
A. A. Jarrett
R. Jones
J. H. Parsons

Group 4—Product Isolation

V. R. Cooper—GROUP LEADER
B. W. Bailey
L. B. Farabee
R. H. Firminhac
L. H. Gevantman
A. J. Green
F. L. Halbach
K. K. Kennedy
M. Lindner
N. A. Spector

Group 5—Basic Chemistry

L. B. Werner—GROUP LEADER
J. R. Dam
J. C. Kroner
G. E. Moore

Group 6—Product Isolation

B. A. Fries—GROUP LEADER
J. Barrick
J. P. Manion

the pile was being processed in the plant at the rate of one-third ton per day; by February 1, 1944, 190 milligrams of plutonium had been isolated; and by March 1, several grams had been produced. This and the following plutonium was of special importance to the Los Alamos Laboratory. The yield from the plant at the very start

was about 50 per cent, and by June 1944 it was between 80 and 90 per cent.

Even though this performance seemed better than expected, many problems remained. Learning to operate the plant most efficiently required some practice, although relatively few operating errors were made. Performance could not be evaluated for some time after a run was finished, when the analytical data became available. Even though an amazingly good job had been done by the design division of the duPont Company, there were a few minor errors in the design of certain equipment. One difficulty in design was that no adequate provision had been made for dissolving the bismuth phosphate precipitates containing plutonium from the walls of the tanks. The early yields were low for this reason, as reflected by low material balances for plutonium through the process. The difficulty was corrected by installing equipment to wash the walls of the tanks with nitric acid to dissolve the precipitates completely. At the same time a change in the order of addition of reagents in the precipitation of bismuth phosphate was made, so that the precipitates were easier to dissolve. Decontamination factors in the process improved at this time also; other improvements in the process and equipment were made continuously during the next few months.

One very important phase of the laboratory work which must be mentioned is the isolation of the plutonium produced in the pilot plant. Even though considerable concentration had been accomplished in the concentration steps of the plant process, and the amounts of plutonium now becoming available were very large compared to those available before, they were much too small to be handled by the plant. Since isolation, then, was essentially a laboratory-scale operation, a group supervised by V. R. Cooper was organized and given responsibility for isolation of the plutonium from the separations-process pilot plant. L. B. Werner made the final isolation and hence was the first man in the world to handle sub-gram and then gram amounts of pure compounds of plutonium. He was aided in this difficult task by B. A. Fries.

Up to this time relatively little attention had been given to the study of isolation methods suitable for use at the Clinton Works. In addition to lanthanum fluoride and plutonium, the material

delivered to Cooper's group contained extraneous insoluble solids, oil and grease, interfering ions such as zirconium (IV), and other impurities concentrated in the fluoride cycles designed to provide for the concentration of plutonium. It is indeed remarkable that approximately 99 per cent of the plutonium received by the isolation group was recovered in substantially pure form.

After the operation of the Clinton extraction plant, and with the use of some of the plutonium thus made available, a complete mechanical test of the Hanford process on the semi-works scale was carried out. This work was done by a number of the chemical engineers working with O. H. Greager and gave information of great value to the ultimate success of the process at Hanford. This work tested the Bismuth Phosphate Process at Hanford concentrations of fission products as well as at Hanford concentration of plutonium (requiring some 10 grams of plutonium).

The successful first and crucial test of the process at the Hanford plutonium concentration had been made somewhat earlier at the Metallurgical Laboratory on the ultramicrochemical scale, using cyclotron-produced plutonium, as described below. A further successful test at this concentration of plutonium was made at the Metallurgical Laboratory on the liter scale of investigation, using Clinton-produced plutonium (as mentioned below, page 67). Such tests of the carrying ability of bismuth phosphate for plutonium (IV), established as the oxidation state which was coprecipitated so efficiently in the tracer experiments, were very necessary in view of the lack of understanding of the mechanism by which the plutonium was incorporated into the bismuth phosphate crystal lattice. It could not be isomorphous incorporation in the lattice because of the difference in oxidation states of the plutonium and bismuth and the different crystal structures of their phosphates. There were many who were convinced that the Process could never work at plant concentrations, some backing their convictions with bets, and a number of those holding these opinions were not convinced until the day the Process was successful in the production plant. The test at the earliest possible time, leading to the ultramicrochemical program of investigation, was vital in order that another process might be chosen in the event the test should indicate failure. This program is described in the following sections.

1.6 Ultramicrochemistry

As mentioned above, although the outline of a chemical separation process could be obtained by tracer-scale investigations, the process could not be defined with certainty until study of it was made possible at the actual concentrations of plutonium that would exist in the large-scale separation plants. Such a test was particularly necessary in view of the poor understanding of the mechanism by which plutonium (IV) is carried by bismuth phosphate and the skepticism of many that the carrying would be observed at the concentrations of plutonium that would exist in the Hanford plant. This test had to be carried out as soon as possible after the discovery of the Bismuth Phosphate Process, and it was performed at the Metallurgical Laboratory in early 1943, following the isolation of plutonium the previous fall.

The question, in the summer of 1942, was as follows: How could any separations process be tested at the concentrations of plutonium that would exist several years later in the production plants when, at this time, there was not even a microgram of plutonium available? This problem was solved through an unprecedented series of experiments encompassing two major objectives. First, it was decided to attempt the production of an actually weighable amount of plutonium by bombarding large amounts of uranium with the neutrons from cyclotrons. It must be remembered that never before had weighable amounts of transmutation products been produced with any particle acceleration machine. Even extending this possibility to the limit, it was not anticipated that more than a few micrograms of plutonium could be produced. The second aspect of the solution of this problem involved the novel idea of attempting to work with only microgram amounts of plutonium but, at the same time, at ordinary concentrations. It was decided to undertake a program of investigation involving volumes of solutions and weighings on a scale of operations much below that of ordinary microchemistry.

By using extremely small volumes it was possible to arrange matters so that even microgram quantities could give relatively high concentrations, and by developing balances of the required sensitivity, micrograms were sufficient for quantitative gravimetric

measurements. The field which embraces the chemical study of material on this minute scale of operation has been given the name "ultramicrochemistry" by P. L. Kirk. The pioneer investigations of Kirk and A. A. Benedetti-Pichler in the fields of quantitative and qualitative analysis on the microgram scale were of the greatest value in providing a background of manipulative techniques for the problem at hand.

I should like to give a brief description of the techniques used on this microgram, or ultramicrochemical, scale of operation. The extremely small volumes, of the order of 10^{-1} to 10^{-5} milliliter, are handled with the help of small, specially constructed, capillary containers, pipettes, burettes, micromanipulators, etc. Liquid volumes in the range quoted are measured with an error of less than

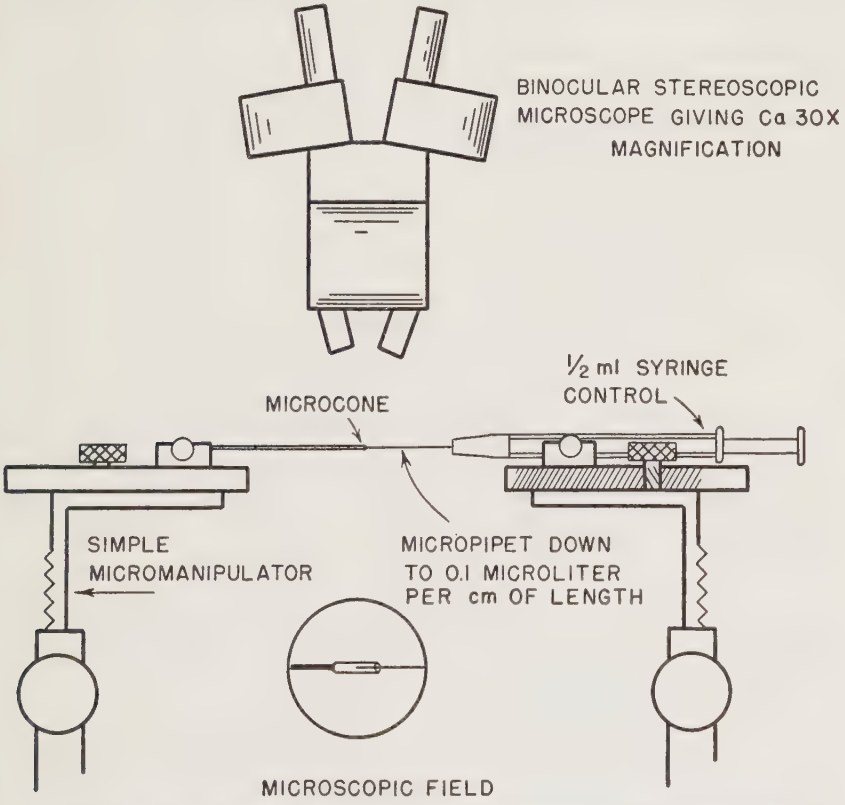


Fig. 1.1 Assembly for studying precipitation reactions on the microgram scale.

one per cent, by means of finely calibrated capillary tubing, the movement of liquid within the capillary being governed by air pressure under sensitive control. The smaller pipettes may be constructed to fill automatically by capillary attraction. The "test tubes" and "beakers" for this work are constructed from capillary tubing that has an inside diameter of 0.1–1 millimeter. The weights of solids which are handled in reagents and precipitates are usually in the range of 0.1–100 micrograms. For purposes of comparison, it is worth mentioning that an ordinary U.S. 10-cent piece weighs about 2.5 grams (2,500,000 micrograms). This ultramicroscale work is usually done upon a mechanical stage of a microscope, where the entire apparatus is within the field of view as illustrated in Fig. 1.1. The test tubes, pipettes, etc. are handled by means of mechanical aids known as micromanipulators. It is very interesting to note that

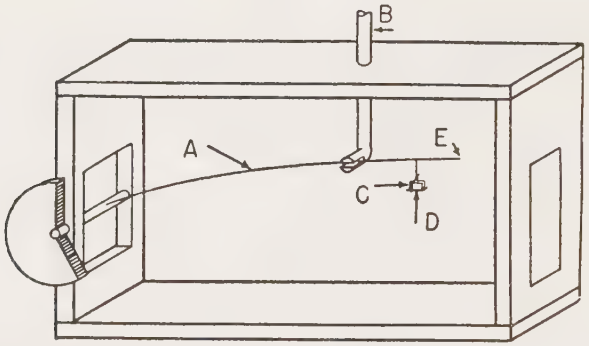


Fig. 1.2 Salvioni balance, with a sensitivity of 0.02 microgram, a weighing range of 20 micrograms, and a capacity of 0.5 milligram. A: quartz fiber (about 4×10^{-3} inches in diameter); B: adjustable stop used in loading; C: aluminum cradle for weighing pan (weight, about 200 micrograms); D: platinum weighing pan (weight, about 150 micrograms; about 1.5×2 millimeters); E: position of fiber read by a reading microscope (accurate to about 0.002 millimeter).

precision of the order of 0.5 per cent is readily obtainable in work on this scale. The separation of solids from liquids is usually done by means of centrifugation rather than by filtration.

One type of balance used in the weighing experiments is the Salvioni balance shown in Fig. 1.2, consisting of a very thin quartz fiber, fastened at one end to a solid base; at the other end is attached, at right angles, a small holder for the sample to be

weighed. The balance is named for the Italian investigator E. Salvioni, who in 1901 used fine glass fibers to weigh small samples of odorous substances to 0.1 microgram in order to determine quantitative limits of olfactory detection. The determination of the weight of the sample depends upon measuring the amount of bending of the quartz fiber arm, and the balance is usually calibrated by weighing solid residues of known weight obtained as the result of the evaporation of aliquot samples of solutions of known compositions.

Another type of ultramicrobalance used in a number of these investigations had an extremely high sensitivity and was designed and built by Kirk, R. D. Craig, and J. E. Gullberg of the University of California. The design of the Kirk-Craig-Gullberg balance was influenced to a considerable extent by the early work on ultrasensitive microbalances by the Australian scientists B. D. Steele and K. Grant, and the work of the Swedish physicist, H. Pettersson. This balance could weigh amounts as small as one microgram or less with an accuracy of 0.02 microgram and is shown in Fig. 1.3. The material could be in a container weighing at least as much as

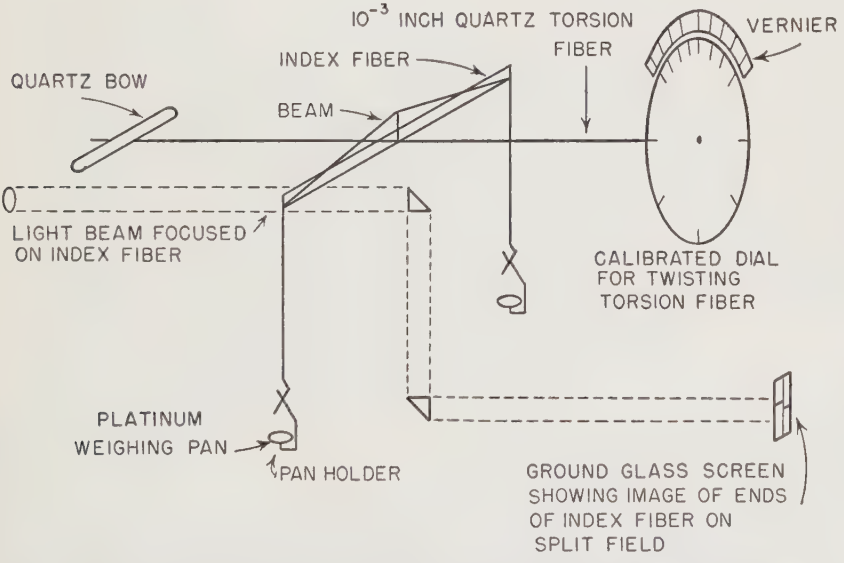


Fig. 1.3 Quartz fiber torsion microbalance, with a sensitivity of 0.02 microgram, a weighing range of 300 micrograms, and a load capacity of 25 milligrams.

25 milligrams, i.e. 25,000 micrograms. The beam and other operating parts of this balance are constructed of fibers of pure quartz ranging in diameter from about four times that of a human hair down to those which are invisible to the unaided eye. The beam of the balance is a quartz fiber framework some four inches in length which is suspended inside a brass housing on a horizontal fiber at right angles to the plane of the beam. From each end of the beam there hangs a fiber, to which is attached a quartz frame holding a weighing pan of thin platinum foil. Objects to be weighed are placed on the foil. The addition of a weight to one side of the balance causes the beam to be depressed on that side. The beam is restored to its initial position by twisting in the opposite direction on the fiber which supports it. The torsion applied in order to return the beam to its initial position, after the addition of a weight, is measured and used to evaluate the weight added. The movement of the beam is magnified by a suitable optical arrangement, and during a weighing all parts of the balance are protected against the slightest air current. In working with this balance and the small amounts of material which were weighed, it was said that "invisible material was being weighed with an invisible balance"!

1.7 Isolation of Plutonium

The isolation of plutonium at the Metallurgical Laboratory, after initial contributions by M. Cefola, was carried on chiefly by B. B. Cunningham and L. B. Werner, who had previously been occupied in the biochemical field. The first pure chemical compound of plutonium, free from carrier material and all other foreign matter, was prepared on August 18, 1942, after starting with a plutonium concentrate in about 10 milligrams of rare earths prepared by A. C. Wahl and co-workers at Berkeley. This historic day marks man's first sight of the element plutonium and, in fact, the first sight of a synthetically produced isotope of any element. The excitement throughout the laboratory, which was situated in a guarded area on the fourth floor of the Jones Chemical Laboratory on the University of Chicago campus, was great indeed, as person after person came to view the historic sight under the microscope. Fig. 1.4 shows a photograph of the room where this work was done;

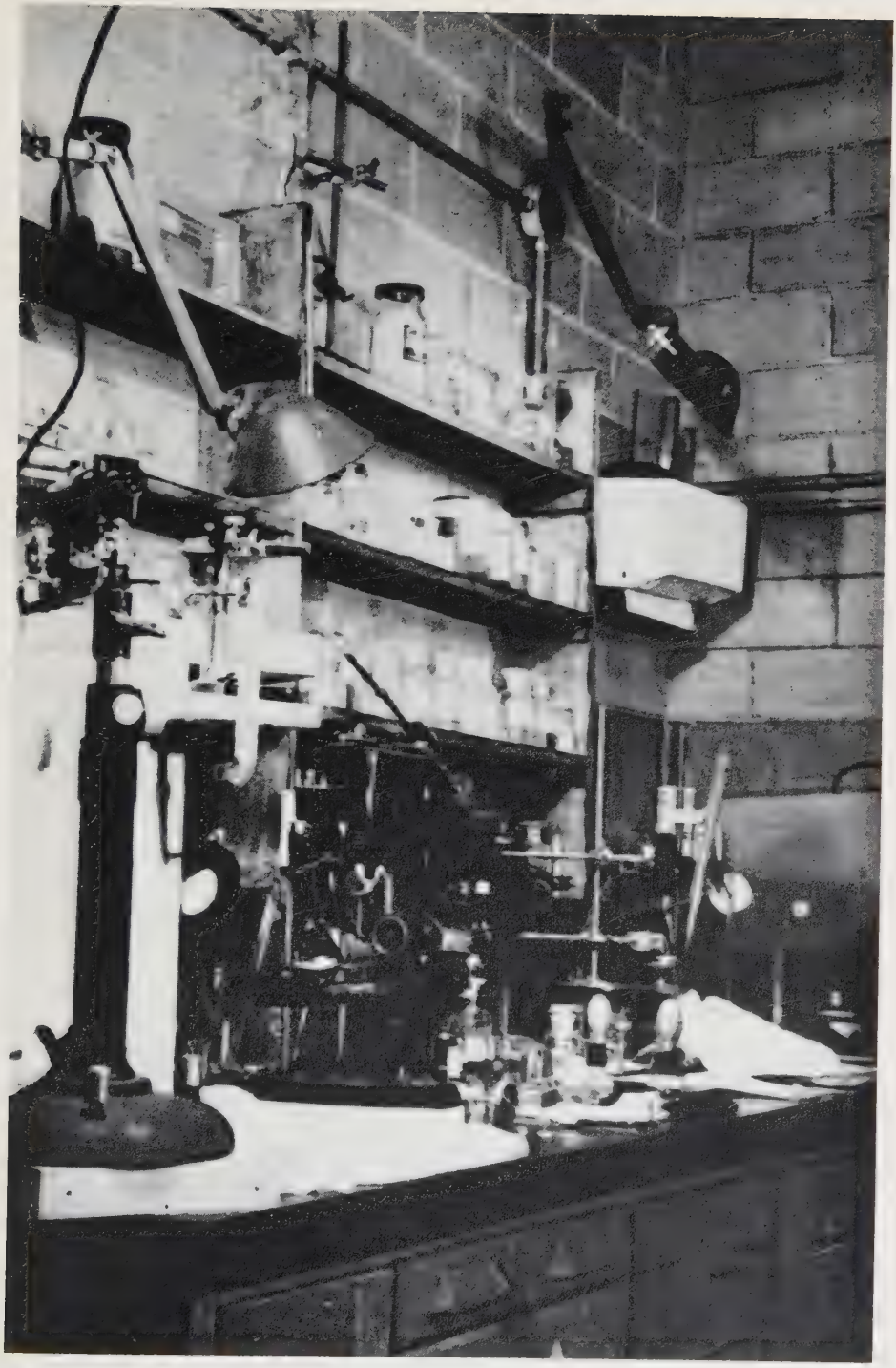


Fig. 1.4 First laboratory for the study of pure plutonium (University of Chicago, fall of 1942).

it had previously served as a balance room and was situated just off the larger laboratory, room number 404. This moment can perhaps be best recaptured by quoting verbatim from the account of the work which appeared in Metallurgical Laboratory Chemistry Report CN-250 for the period August 16–31, 1942:

Ultra Microchemical Investigations on 94

A. *Isolation of compounds of pure element 94.* In our last report, (CN-239) we described our preparations for experiments with pure element 94, in which the 30,000-year 94^{239} is to be used. Although larger amounts of 94^{239} will be available soon, we had on hand about 1 μg for immediate experimentation. Using this quantity of 94^{239}, we have prepared some compounds of *pure element 94.* The sample containing this 94^{239}, which originally had about 10 mg of rare earths (Ce^{+4} and La^{+3}) with it as carrier, was carried through a series of oxidation-reduction cycles using fluoride precipitations and Ag^{++}, $S_2O_8^{--}$ oxidations. In four such cycles, the amount of carrier was successively reduced from 10 mg to 1 mg to 20 μg to 5 μg, and finally to 0 μg, with the interpolation of a hydroxide precipitation at the 5 μg of carrier stage. The volumes in which precipitation took place in the last three steps were from 100 to 15 λ, and only La^{+3} was used as carrier in these steps.

B. *Precipitation of 94 as fluoride or double fluoride.* After all of the rare earth carrier had been eliminated as described above, the fluoride, or perhaps a double fluoride, of *pure element 94* was precipitated by adding HF to the solution in which 94 was present in its lower oxidation state. This precipitate of 94 which was viewed under the microscope and which was also visible to the naked eye did not differ visibly from the rare earth fluorides. (Shortly after the 94 was precipitated, a considerable quantity of K_2SiF_6 was observed to separate as a result of the fact that precipitation had been performed in glass vessels. This will be avoidable in future work because we have now developed suitable fluoride-resistant micro vessels.)

From the alpha-activity remaining in the supernatant liquid after the final precipitation as a fluoride, it can be calculated, using 30,000 years as the half-life of 94^{239}, that this salt of 94 has a solubility of the order of magnitude of 10 mg of the element per liter of 6 N HF solution. This value is necessarily somewhat tentative.

C. *Precipitation of 94 as iodate.* The mixed precipitate of 94 fluoride and K_2SiF_6 was treated with H_2SO_4 and heated to the appearance of fumes of SO_3. Because of the large volume of water required to dissolve the residue, 20 μg of La^{+3} were added as carrier and mixed $La(OH)_3$ and 94 hydroxide were precipitated. This was dissolved in a minimum volume of

6 N H_2SO_4. In this operation some of the La^{+3} as $La_2(SO_4)_3$ failed to dissolve, and this was centrifuged off. Excess potassium iodate was added to the filtrate and mixed iodates of 94 and Ag^+ (the Ag coming from traces of silver oxide which had precipitated with the hydroxides) were obtained. The silver iodate was dissolved away from the precipitate by using 6 N NH_4OH, which was subsequently removed. A small amount of brownish crystalline precipitate remained, and upon treatment with a little H_2O_2 in ~3 N HNO_3 and $\frac{1}{4}$-saturated KIO_3, the color of this precipitate changed to white without any other visible change in its characteristics. This remaining precipitate presumably was the iodate of *pure element 94*. From the alpha-activity remaining in the supernatant liquid in equilibrium with the 94 iodate, it appears that the iodate in $\frac{1}{4}$-saturated KIO_3 solution in ~3 N HNO_3 has a solubility of the same order of magnitude as the fluoride or somewhat less. This value also is a tentative one.

Accurate data on the solubility of pure compounds of pure element 94 will be available from our experiments shortly.

It should be noted that at the time this was written the element was often referred to as "element 94" or simply as "94." The name "plutonium" had been given it only a few months earlier and was not yet in general use on the Project. Also it might be mentioned that the code name "49" was by this time being used to designate the isotope 94^{239}, following the general (not very subtle) system which used the last digits of the atomic and mass numbers to represent an isotope.

The first weighing of a pure compound of plutonium occurred on September 10, 1942, when 2.77 micrograms of the oxide (PuO_2) were weighed by Cunningham and Werner. It was part of the plutonium, mentioned below, produced in the large undertaking of the summer of 1942. A picture of this original oxide—carefully preserved and placed on exhibition at the United Nations Conference on the Peaceful Uses of Atomic Energy at Geneva in 1955—is shown in Fig. 1.5. A second, 4.45 microgram, sample was used for a specific activity measurement, as described below. Again the best understanding of these original experiments, including the first manipulations of the pure element in and out of aqueous solution, will come from reading the following verbatim quotation from Metallurgical Laboratory Chemistry Report CN-261 for the period September 1–15, 1942, where the work was described at that time:

Fig. 1.5 This highly magnified plutonium compound (2.77 micrograms of oxide) is the first to be weighed by man (September 10,1942) and is here shown on a platinum weighing boat. The picture is magnified approximately 35-fold. The plutonium oxide appears as a crusty deposit (indicated by the arrow) near the end of the platinum weighing boat, which is held with forceps that grip a small handle (upper part of photograph).

Ultra Microchemical Investigations on 94

Introduction. In our last report (CN-250), we described the isolation of compounds of essentially pure 94^{239}. Further work which is described in this report has been done upon the isolation of larger amounts of 94^{239}. This larger amount of 94^{239} has made it possible to investigate the properties of some of the compounds of 94 and the results of this investigation are described in this section. The method of purification used in order to obtain the pure 94^{239} is described immediately below.

A. *Isolation and purification of plutonium.* A sample containing plutonium equivalent to 8×10^6 alpha disintegrations per minute, in a volume of 18 cc, was treated with 1 mgm La^{+3} carrier, and mixed La and 94 fluorides precipitated by the addition of HF. The fluorides were dissolved by heating with H_2SO_4 to the appearance of fumes of SO_3. The sulfate solution was taken up in a volume of approximately 1 ml, made 1 M in HNO_3, saturated with $(NH_4)_2S_2O_8$ and treated with approximately 5 mgm AgO. After 10 minutes, the solution was made 6 M in HF and the precipitated LaF_3 centrifuged out. Two drops of 30% H_2O_2 were added to reduce the 94 and then 100 γ La^{+3} carrier was added. The solution was centrifuged after 30 minutes. The mixed fluorides of La and 94 were dissolved as before, taken up in $\sim$250 λ of H_2O, oxidized as above, and the La^{+3} again precipitated out. The supernatant liquid was transferred to a platinum microcrucible, treated with a few drops of 6 N H_2SO_4, and the fluoride expelled by heating in the usual way. The H_2SO_4 digest was treated with 5 drops of concentrated NH_4OH, and the resulting hydroxide precipitate packed by centrifugation in a micro cone. The hydroxide was washed 3 times with approximately 40-λ portions of concentrated NH_4OH (in order to remove any silver). The hydroxide was then dissolved in a minimum volume of concentrated HNO_3, and the iodate was precipitated from this solution by the addition of an excess of saturated KIO_3 solution. The iodate was washed 3 times with 6 M HNO_3 $\frac{1}{4}$-saturated with KIO_3 (to remove the La impurity) and was then converted to the chloride by several evaporations with 6 M HCl. The chloride was converted to the nitrate by repeated evaporation with concentrated HNO_3. The hydroxide was precipitated once more with concentrated NH_4OH, the supernatant liquid removed, the nitrate formed by adding HNO_3 and a portion of this nitrate was converted to the oxide by ignition. The oxide was weighed and its specific alpha-activity determined. Assuming the formula of the oxide to be PuO_2, a specific activity of 110,000 alpha disintegrations per minute per microgram Pu was found. The rest of the plutonium nitrate solution was then treated with concentrated NH_4OH, the hydroxide washed 3 times as before, then converted to the iodate and again washed 4 times with 6 M HNO_3-iodate solution. The oxide (assumed PuO_2) prepared from this compound showed a specific activity of 167,000 disinte-

grations per minute per microgram Pu (see section H), and it was considered probable that the plutonium was reasonably pure.

B. *Plutonous nitrate.* Using some of the pure plutonium whose purification is described in the section above, pure solid plutonous nitrate was prepared. This compound was prepared by the evaporation of a concentrated solution of the metal with excess HNO_3. The resulting solid was a lemon-yellow crystalline material, probably deliquescent and hydrated. It melted easily on warming. The formula is presumably $Pu(NO_3)_4 \cdot xH_2O$. Solutions of plutonous nitrate of concentrations about 2–4 grams plutonium per liter appear pale yellow-green in color.

C. *Plutonous oxide.* This compound was prepared by ignition of the plutonous nitrate. This compound was yellow-brown in color; crystalline form was not evident. It was virtually insoluble in 6 N HNO_3 either at room temperature or at boiling temperature. It dissolved fairly readily in hot concentrated H_2SO_4, presumably due to the formation of the stable soluble complex of Pu^{+4} with sulfate (Reports CN-239 and CN-250). It also dissolved in 6 N HNO_3 when Ce^{+4} was present, presumably being aided by the oxidation of the Pu^{+4} to its higher oxidation state. The formula may very well be PuO_2.

D. *Plutonous iodate.* This compound was formed by precipitation upon addition of KIO_3 to a plutonous nitrate solution. The precipitate was a white, bulky crystalline material. The solubility in a solution 6 N in HNO_3 and containing approximately 4 g KIO_3/liter is about 0.020 grams plutonium per liter. The solubility was determined from the alpha-activity remaining in solution after the precipitation of the plutonous iodate. This is a *practical* solubility and may not necessarily be a *true* solubility, since there is no assurance that equilibrium had been attained between the two phases. The formula, again upon the assumption that the lower oxidation state has an oxidation number of +4, is presumably $Pu(IO_3)_4$.

E. *Plutonous hydroxide.* This was prepared in these experiments by treating the iodate with concentrated NH_4OH. The more insoluble plutonous hydroxide was formed and from the alpha-activity remaining in the solution after this transformation it can be deduced that the solubility corresponds to 0.004 grams plutonium per liter. Again there is no assurance that this is the true solubility, in that it was not certain that there was equilibrium between the two phases. The plutonous hydroxide, presumably of formula $Pu(OH)_4 \cdot xH_2O$ appeared as a pale yellowish-green flocculent precipitate. Figure A (not reproduced here) shows a positive photo-micrograph of about 0.5 γ of Pu as the hydroxide under a magnification of approximately 30 diameters taken with reflected light. The dark material in the photograph is the glass micro centrifuge cone in which the precipitate appears as a white mass which is slightly dislodged from the barely discernible apex of the centrifuge cone.

F. *Plutonous fluoride.* This has not yet been prepared in a completely

pure state. Plutonous fluoride is, however, very insoluble, and appears as a white (or pale yellow) flocculent precipitate.

G. *Plutonium peroxide.* This compound was prepared by precipitation from a plutonous chloride solution which had in turn been prepared by dissolving plutonous hydroxide in HCl and evaporating to dryness. After the solution of the chloride in about 20 mλ of distilled water, excess H_2O_2 was added. A small white precipitate (perhaps slightly yellow) rather more crystalline than the hydroxide, appeared. On the basis of this experiment, the plutonium peroxide appears to be insoluble, although further experiments under controlled pH conditions are necessary to make the information useful.

H. *Half-life of* 94^{239}. A sample of plutonous oxide, obtained by igniting the nitrate described in section B at about 700°C for 20 minutes was weighed on the Salvioni balance by the technique previously described (Report CN-239). 4.45 γ of the oxide (assumed PuO_2) showed an alpha-activity of 672,000 disintegrations per minute. The activity per microgram of plutonium was calculated as 167,000 disintegrations per minute. From this determination the half-life of Pu would appear to be 20,000 ± 2000 years. Additional purifications and determinations of the specific activity will be necessary before this figure can be considered as final.

During this early period when visible amounts of plutonium were being precipitated, numerous visitors came to our laboratory to have a look at the fascinating new element. With the supply so limited and the experiments to be performed so many, it was not possible to keep much material immobilized to show them. It is, therefore, with some hesitation that we may now confess that some of the hydroxide samples which were placed on view consisted of the much more available aluminum hydroxide colored with green ink; it should be understood, however, that great care was taken on all such occasions to remark, "This *represents* a sample of plutonium hydroxide," a statement which was often misunderstood to mean that it was actually a sample of plutonium hydroxide which was on display. One especially auspicious occasion found General Leslie R. Groves in our laboratory to look at the valuable new substance. The sample, in this case, the real and precious plutonium hydroxide, was lined up under the microscope with the greatest of pride, and the disappointment was very great when he made the remark, "I don't see anything."

During the summer of 1942, large amounts of uranium (hundreds of pounds) were bombarded for several months with the

neutrons from the cyclotrons of the University of California, Berkeley, under the supervision of J. G. Hamilton; and Washington University, St. Louis, under the supervision of A. S. Langsdorf, Jr. The initial large-scale operations at the Metallurgical Laboratory for the isolation of plutonium were carried out by T. P. Kohman and A. H. Jaffey and co-workers. In these operations diethyl ether was used to separate the bulk of the uranium, as uranyl nitrate hexahydrate from the plutonium (IV) and fission products; it is the success of this method that led to the above-mentioned consideration of solvent extraction as a possible chemical procedure to be used in the manufacture of plutonium. The lanthanum fluoride oxidation-reduction procedure was used for the separation of the plutonium from the fission products and for its concentration. These operations resulted in the production of several hundred micrograms of plutonium, a great deal more than had been anticipated. This was used in the tracer-scale investigations of the chemical separation processes for plutonium and other tracer-scale investigations of plutonium, and also made it possible to carry on the program of ultramicrochemical investigation at Chicago (including the work described just above). In September 1942 B. B. Cunningham and L. B. Werner were able to prepare a number of compounds of pure plutonium and to determine with certainty, by means of chemical analysis, that the oxidation number of the most stable state of the element in solution is the IV state. M. Cefola, R. L. Patton, and C. Smith also made contributions to the program at the Metallurgical Laboratory, at this time as well as somewhat later.

The group remaining in Berkeley with W. M. Latimer also contributed to this ultramicrochemical program of investigation. During the summer of 1942, A. C. Wahl, independently, was also processing cyclotron-irradiated uranium in order to isolate pure plutonium. He succeeded in isolating 200 micrograms of chemically pure plutonium in 92 per cent yield from 45 kilograms of uranium that had been irradiated for two months with neutrons from the Berkeley 60-inch cyclotron. He employed the Lanthanum Fluoride Process and measured yields and decontamination factors at every step, collecting data which proved very valuable in evaluation of

this separations process, then the only practical method for isolation of plutonium. The chemistry was started in July, but progress was slow because of the care exercised in evaluation of the separations process, and a pure compound of plutonium, plutonium (IV) hydroxide, was not isolated until September 29, 1942. However, it was with great elation that Wahl showed the 0.2 milligram plutonium sample, easily visible to the naked eye, to E. O. Lawrence, whose cyclotron had produced the plutonium. This plutonium was used in an ultramicrochemical program of investigation at Berkeley, by Wahl, J. W. Gofman, J. W. Hamaker, G. E. Sheline, and W. H. McVey. Among other accomplishments, this group was able to establish in 1943 that the oxidation number of the highest state is VI.

From this time until the fall of 1943, cyclotron bombardments were the sole source of plutonium, and over this period of time about 2,000 micrograms, or 2 milligrams, of plutonium, were prepared. This material was used to maximum advantage by the ultramicrochemists to prepare compounds of plutonium and to measure properties such as solubilities and oxidation potentials. In particular, it was possible—and this was of inestimable importance —to test the Bismuth Phosphate Process which was under consideration for use at Hanford. The various parts of the complicated separation and isolation procedures were tested at the Hanford concentrations of plutonium in the careful and crucial experiments performed by B. B. Cunningham, L. B. Werner, D. R. Miller, I. Perlman, and others. Without the possibility of these tests early in 1943, I believe it is fair to say that this process, which went into use at Hanford and turned out exceedingly well, would not have been chosen.

I want to emphasize that the scale-up between the ultramicrochemical experiments to the final Hanford plant amounts to a factor of about 10^9, surely the greatest scale-up factor ever attempted. In spite of these difficulties the chemical separations process at Hanford was successful from the beginning, and its performance exceeded all expectations. High yields and decontamination factors (separation from fission activity) were achieved in the very beginning and continued to improve with time.

1.8 The Hanford Plant

Northwest from the village of Pasco in southeastern Washington, the Columbia River makes a ninety-degree bend around a flat, arid expanse of land, which is bounded on its other two sides by high hills. Within this 600-square-mile area lie the several plants that make up the plutonium-manufacturing Hanford Engineer Works, known during wartime by the code name "Site W." The site was chosen with especial care for the needs of this unique enterprise. The mild winters and negligible rainfall allowed unimpeded construction the year around. The mighty Columbia River provides in necessary amounts the low-temperature water to cool the chain-reacting piles. Flanking the area at convenient distances are the Grand Coulee and Bonneville power networks.

Not least among the considerations in choice of site was the remoteness of the region from centers of population, a necessary forethought should unforeseen events have allowed the chain reactions to get out of control or the chemical plants to spew forth their contents, which are almost inconceivably high in radioactivity. It is a tribute to the painstaking care in planning that this massive undertaking offered the safest of industrial jobs to the operators.

The construction camp for the plant was built at the site of the village of Hanford, from which the plant draws its name. At one time over 50,000 people lived in trailers and barracks at Hanford, but with the completion of construction work it was completely evacuated. At a greater distance from the plant site a new village of permanent dwellings to house the plant operators was built at the location of the existing village of Richland.

There are two principal types of plants at the Hanford Engineer Works: those that form the plutonium within the uranium by a nuclear chain reaction, and those that separate the plutonium from the uranium and the fission products. The former consist of water-cooled piles, cooled by the circulation of treated Columbia River water. The huge separation units are strictly chemical plants, operated, like the piles, by remote control.

The Hanford site had been examined at the end of 1942 and was acquired by the government early in 1943. Construction of the piles began on June 7, 1943. By the spring of 1944 construction

of the chemical plants was well under way and duPont personnel were maintaining contact with developments at Wilmington, Chicago, Clinton, and Hanford. One of these men, L. Squires (who had participated in early process development work), kept himself closely informed of all developments at the various sites and expertly coordinated efforts in process improvement and equipment design. Blueprints of the equipment to be used at Hanford were constantly being submitted to representatives of the Metallurgical Laboratory for examination and approval or suggestions for improvement. The canning problem (i.e. the problem of sealing the uranium in protective metal jackets) was a critical one. It was definitely not a simple matter to find a sheath that would protect uranium from water corrosion, keep fission products out of the water, transmit heat from the uranium to the water, and at the same time not absorb too many neutrons, but the problem was solved.

Prominent in the design of the various parts of the Hanford plant were R. P. Genereaux, F. W. Pardee, and S. L. Handforth, while F. H. MacKie, G. P. Church, and R. K. Mason were leaders in the construction phase. W. A. Dew was responsible for training the Hanford production personnel. W. O. Simon was plant manager during the start-up and initial operation, and among his staff were such able people as D. O. Notman, B. H. Mackey, S. J. Bugbee, E. E. Swenson, W. C. Kay, L. Squires, F. A. Otto, and M. H. Smith. During the spring and summer of 1944 many technical personnel began to move to the Hanford site. These again included physicists, chemists, engineers, and others needed to ensure the success of the operation in a Technical Area. C. W. J. Wende, P. F. Gast, W. R. Kanne, and others played important roles in the field of physics. W. P. Overbeck made important contributions to the development of many of the electrical instruments that were needed. D. M. Smith headed an analytical division, and R. E. Curtis led a development group in this division. P. L. Kirk and co-workers developed methods of microchemical analysis of control samples, thus avoiding some of the hazards of working with large samples of the extremely radioactive process solutions. N. Hilberry, I. Perlman, and J. P. Howe represented A. H. Compton and the Metallurgical Laboratory, while H. Worthington, W. K. Woods,

T. B. Drew and J. A. Wheeler represented C. H. Greenewalt and the duPont Wilmington office in connection with important liaison and advisory work concerned with critical parts of the program.

The chemical process investigations in the Technical Area were under the direction of J. E. Willard. Willard's organization was recruited from duPont, Metallurgical Laboratory, and Clinton Laboratories personnel and was composed of chemistry groups under the supervision of J. H. Peterson, S. G. Thompson, D. R. Miller, C. M. Olson, W. H Sullivan, and G. W. Watt. An organization chart for the groups working under Willard, corresponding to a period late in 1944, is shown in Table 1.3. Plant assistance groups under O. H. Greager and M. F. Acken included numerous chemical engineers who had had long association with the process development work, e.g. R. S. Apple, R. H. Beaton, L. C. Peery, D. S. Webster, E. R. Gilbert, and J. B. Work. A semi-works group operated under the direction of I. D. Chambers and, later, W. W. Armstrong. In addition to the performance of assignments involving a continuation of process development work, the chief purpose for the transfer of these groups to Hanford was to provide expert advice and assistance in the event of serious chemical or operational difficulties at the Hanford plant. Similarly, personnel remaining at Clinton and Chicago provided a reserve of technical manpower available for diversion to work on Hanford problems in case of necessity.

Operation of the first pile began in September 1944, following some initial trouble caused by the absorption of neutrons in the fission product Xe^{135}, and the first production run of Hanford material in a separations plant began on December 26, 1944. The final operating standards for the Bismuth Phosphate Process, based on recommendations of the Clinton Laboratories, were reviewed at Hanford by a delegation from the Metallurgical Laboratory during December 12 to 15, 1944, and had just been finally approved on December 15, 1944. As had been true in the early operation of the pilot plant at Oak Ridge, a number of minor operational difficulties were encountered, and certain modifications in sampling methods and analytical procedures were required. The yields in the first plant runs, which took place in December 1944, and January 1945, ranged between 60 and 70 per cent, reached 90 per cent early in

TABLE 1.3 *Organization Chart of Process Chemistry Section, Hanford Engineer Works (late 1944)*

J. E. Willard—AREA SUPERVISOR
J. H. Peterson—ASSISTANT AREA SUPERVISOR

Group 1—Process Research

S. G. Thompson—SENIOR SUPERVISOR
R. P. Black
J. L. Dreher
O. F. Hill
H. J. Kamack
W. J. Knox
H. T. Siefen

Group 2—Fission Products

W. H Sullivan—SENIOR SUPERVISOR
N. E. Ballou
T. P. Kohman
G. Leader
D. C. Lincoln
J. A. Swartout

Group 3—Process Development

C. M. Olson—SENIOR SUPERVISOR
A. H. Angerman
B. F. Faris
W. L. Kay
B. H. Perkins
W. F. Schneller
G. W. Stahl
E. H. Turk

Group 4—Product Isolation

G. W. Watt—SENIOR SUPERVISOR
V. R. Cooper
B. A. Fries
R. Goeckerman
M. Lindner
D. G. Pye
F. R. Yett

Group 5—Heavy Element Chemistry

D. R. Miller—SENIOR SUPERVISOR
S. R. Gaarder
H. R. Hoekstra
W. C. Johnson
G. W. Sears
L. B. Werner

February 1945, and were up to 93 per cent by early summer and above 95 per cent soon thereafter. From the very beginning decontamination factors were better than anticipated and reached the over-all value of 10^8. The first delivery of plutonium to the Los Alamos Laboratory occurred on February 2, 1945.

The chemical plants were massive structures ingeniously engineered to fit the grave problems inherent in handling the extremely high levels of radioactivity. It is self-evident that no one saw the plutonium as it entered the plant. It is also true that no one saw it until just before it finally emerged as a relatively pure compound.

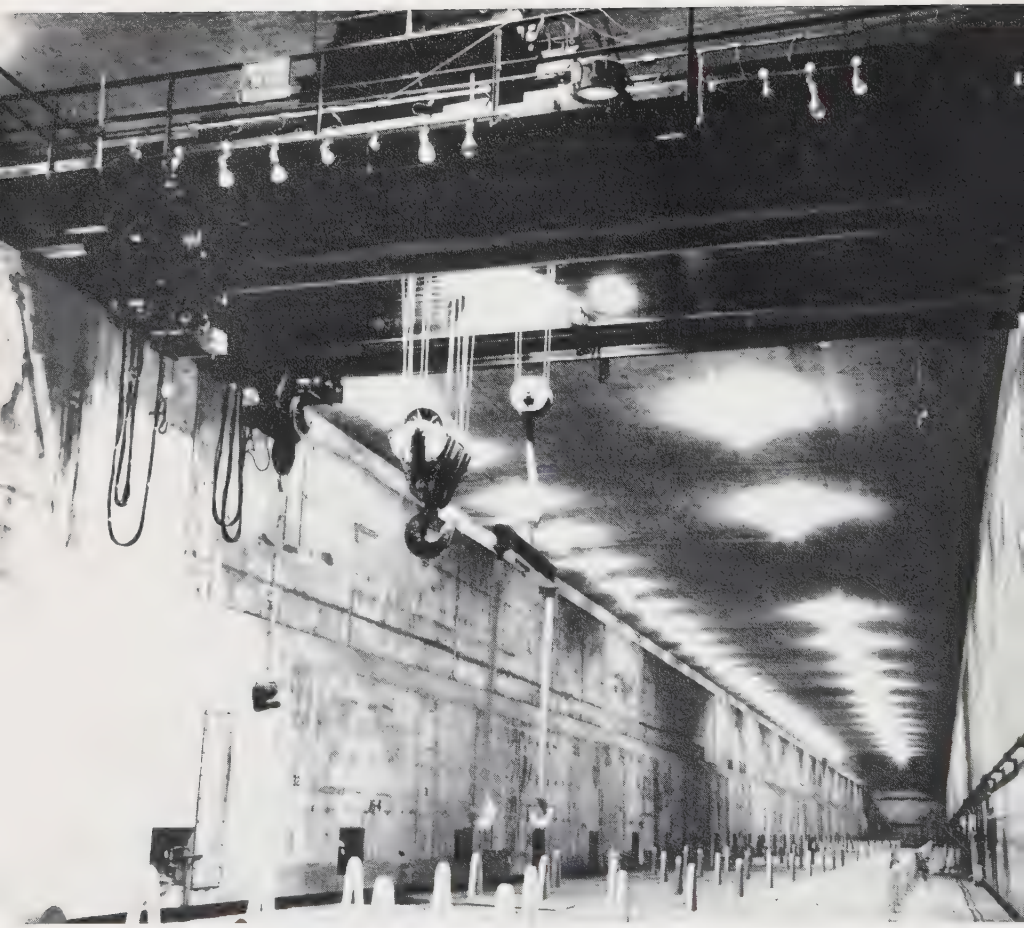


Fig. 1.6 View of Hanford Chemical Extraction Plant in which Bismuth Phosphate Process was used.

In the meantime, it had passed through a maze of reaction vessels via thousands of feet of piping with only instruments and an occasional sampling to chart its progress. Probably no process on a grand scale in chemical-engineering history received such painful care in its development and engineering designs as that operating in the Hanford plutonium plant, certainly not in such a brief span of time.

Fig. 1.6 shows a picture of one of the chemical extraction plants at the Hanford Engineer Works in which the Bismuth Phosphate Process was used. This view is taken right in the "canyon" area where no one could be present when the process was operating. The actual operating cells containing the centrifuges and other apparatus are below the open area; the handles for lifting the covers to the concrete "cell blocks" can be seen. The remote-control operating gallery is behind the thick concrete wall to the left. The crane which was used for the remote-control lifting and replacing of equipment when the cell block covers were removed is shown above. The remote-control operated cask car for the transport of material enters the canyon at the far right.

1.9 The Los Alamos Laboratory

The responsibility for making a weapon out of the plutonium produced at Hanford (and out of the U^{235} produced at Oak Ridge) fell to the Los Alamos Laboratory in New Mexico, located on a mesa about 30 miles from Santa Fe. Unfortunately, very little has been written about the details of the scientific work which took place at this installation. The present author is not in a position to write an authoritative account of this phase of the plutonium story. However, because the present review would be so incomplete without some word about this important part of the story, a brief description will be attempted.

The Los Alamos Laboratory, known by the code name of "Site Y," was operated (and still is operated) by the University of California. As is well known, the wartime director was J. R. Oppenheimer. Consideration of methods for constructing the weapon began as early as the summer of 1942 in Berkeley. The Los Alamos

site for the Laboratory was chosen in November of 1942, and by March of 1943 Oppenheimer and some of the members of his research team had moved there. The Laboratory grew to the point where it included hundreds of scientists, recruited from all the other sites of the Manhattan District as well as from many other places. By 1945 this Laboratory had the highest priority with respect to personnel, as well as in other respects, and an extraordinarily capable staff had been assembled. At this time the organization included the following divisions: Experimental Nuclear Physics under R. R. Wilson; Theoretical Physics under H. A. Bethe; Chemistry and Metallurgy under J. W. Kennedy, with C. S. Smith having special responsibility for metallurgy; Explosives under G. B. Kistiakowsky; Ordnance under Captain W. S. Parsons (U.S.N.); Bomb Physics under R. F. Bacher; and Advanced Development under E. Fermi. Fermi and S. K. Allison, who assisted Oppenheimer in the coordination of the research effort, had moved to Los Alamos from the Metallurgical Laboratory in 1944 after the problems connected with the production reactors had been solved.

It was necessary to measure the fission and neutron-capture cross sections of Pu^{239} and the uranium isotopes, the elastic and inelastic neutron cross sections for numerous nuclei, the number, energy, and time of emission of the neutrons emitted in fission, spontaneous-fission rates, and numerous other nuclear constants. It is not possible in the scope of this discussion to do more than mention some of the individual contributors. J. H. Manley was concerned with the measurement of critical neutron cross sections. J. H. Williams and H. H. Staub measured neutron fission cross sections and the energy spectrum of the neutrons emitted in fission. E. Segrè and D. E. Nagle measured the ratio of neutron capture to fission in plutonium. R. R. Wilson made important measurements on the time of fission and other details of this process. R. W. Dodson, Segrè, and A. C. Wahl were concerned with the products formed by the irradiation of Pu^{239} with neutrons. Of especial importance was the discovery by O. Chamberlain, G. W. Farwell, and Segrè (with later contributions by C. E. Wiegand) that Pu^{240}, present in Hanford plutonium as the result of the absorption of neutrons in Pu^{239}, undergoes spontaneous fission at a relatively high rate.

Crucial questions, upon the answers to which the successful use of plutonium in a weapon depended, were whether Pu^{239} emitted neutrons when it underwent fission, and the number of such neutrons emitted. These questions had to be answered early, before any Pu^{239} was available from the reactors. Most of the supply of our chemistry group at the Metallurgical Laboratory was loaned in the summer of 1943 to Los Alamos for the purpose, and their initial measurement was made with this sample containing a few hundred micrograms. In returning the sample to the Metallurgical Laboratory, advantage was taken of my presence in Santa Fe on a short vacation trip in order to save the time which would have been lost in a cumbersome official transfer of the material. Wilson met Mrs. Seaborg and me at breakfast at about 5:00 A.M. in a Santa Fe restaurant, having escorted the sample from Los Alamos with the implied protection of a high-powered rifle; I then transported it by train in my suitcase, without firearms, back to the Chicago Laboratory.

The Chemistry and Metallurgy Division was responsible for the final purification of the Pu^{239} (and U^{235}), for fabrication of the weapon, including the core and tamper, and for various other matters. People working under the direction of J. W. Kennedy, such as A. C. Wahl, C. S. Garner, R. B. Duffield, D. Lipkin, S. I. Weissmann, M. L. Perlman, and others, were principally concerned with plutonium chemistry as applied to plutonium purification; these requirements were very stringent, especially with respect to light-element impurities. I. B. Johns, Jr., H. A. Potratz, and F. K. Pittman were among the others who made important contributions. The remarkable feat of preparing pure plutonium metal and determining its important properties, using milligram and gram amounts, was accomplished under the direction of C. S. Smith, with E. R. Jette, R. D. Baker, M. Kolodney, E. F. Hammel, Jr., and others making important contributions. C. H. Thomas, with the help of J. C. Warner and J. H. Lum acted as a coordinator and advisor in the plutonium chemistry and metallurgy program.

The Theoretical Division included a number of very able men, such as H. A. Bethe, R. F. Christy, E. Teller, R. P. Feynman, R. Serber, and V. F. Weisskopf. Among the problems considered were the determination of the critical size of the fissionable mate-

rial in the weapon, the initiation of the explosion by stray neutrons, the rate of neutron density increase and other changes during the explosion, the equation of state of matter at high temperatures and pressures, and the general problem of how to proceed from data obtained with small quantities of materials to estimates as to what would happen in the weapon. The work of the Ordnance, Explosives, and Bomb Physics Divisions was, of course, concerned with the practical details of designing and building a practical weapon.

Thus it can be seen that the solution to the problem of translating the plutonium, as received in solution from the Hanford Plant, into a workable weapon depended on the work of many men in many different fields. Some of these, of course, were more concerned with the final design and assembly of the weapon and made their most important contributions to this final and most crucial stage of the development. The actual building of the plutonium weapon required many ingenious and brilliant ideas of a fundamental type and important ideas for the details of design. Among those who made contributions in connection with the successful fabrication of the plutonium weapon are L. W. Alvarez, R. F. Bacher, K. T. Bainbridge, Christy, C. L. Critchfield, Feynman, L. H. Johnston, Kistiakowsky, E. M. McMillan, S. H. Neddermeyer, and R. E. Peierls.

1.10 Some Other Early Contributors

1.10a Metallurgical Laboratory

After the initial major emphasis on the separations process work, the research of the chemistry group at the Metallurgical Laboratory took on a broader aspect. Until the successful operation of the chain reactor and chemical separation plants, first at Clinton and then at Hanford, the work continued on the tracer scale and on the ultramicrochemical scale of investigation. After plutonium became available in larger amounts from these plants, it was possible to extend the scope of all of these investigations.

The group of chemists at the Metallurgical Laboratory at the University of Chicago continued to make basic solution and dry chemistry studies, under the direction of B. B. Cunningham, and

plutonium purification studies, under the direction of E. F. Orlemann. Further work on the plutonium separation and decontamination problem was carried on under the direction of S. G. Thompson, in groups under the leadership of F. W. Albaugh, J. L. Dreher and G. W. Watt. This effort came under the direction of Albaugh when S. G. Thompson went to Hanford, and involved groups under R. C. Thompson, J. R. Gilbreath, and S. Lawroski. Investigation of the potentialities of U^{233}, which had been carried on under the direction of R. W. Stoughton was continued in a group under the leadership of L. I. Katzin. I was assisted at various times in the direction of this entire effort by J. E. Willard, W. M. Manning, and Watt. (After the war, Manning became the Director of the Chemistry Division and continues to serve in that capacity in the Argonne National Laboratory.) The personnel changed continually as the people went to the various sites, so that it is difficult to give a short description of the problems which were studied and those who were involved. Perhaps the best summary can be given by showing the organization charts for two periods in the time interval between the early work described above and the end of the war. Table 1.4 shows such an organization chart corresponding to early 1944, while Table 1.5 shows one for about a year later.

In addition to the need for work with pure plutonium in connection with the separations process, it was necessary to determine a number of the physical and chemical properties of the dry salts of plutonium and of plutonium metal. Therefore, the study on the ultramicroscale had to encompass this field of investigation also. A number of compounds of plutonium were prepared by reactions involving the solid and gas phases—that is, by dry chemical reactions. This work was done in collaboration with W. H. Zachariasen and R. C. L. Mooney of the University of Chicago staff, who were able to use the diffraction technique to identify or help identify a number of the compounds that were synthesized and, in many cases, thus to establish their chemical structures. This preparative work and measurement of properties, as well as, later, the use of larger amounts of plutonium from the reactors, was under the direction of an extraordinarily able group of chemists whose accomplishment seems all the more remarkable in retrospect, considering

TABLE 1.4 *Organization Chart of Section C-I, Metallurgical Laboratory (early 1944)*

G. T. Seaborg—SECTION CHIEF
E. E. Smith—SECRETARY TO SECTION CHIEF
K. Buehler—GENERAL SECRETARY TO SECTION
W. M. Manning—ASSOCIATE SECTION CHIEF
G. W. Watt—ASSOCIATE SECTION CHIEF
J. E. Willard—ASSOCIATE SECTION CHIEF
L. I. Katzin—ASSISTANT TO SECTION CHIEF
I. N. Saxton—SECRETARY TO ASSOCIATE SECTION CHIEFS

Sub-Section I—Separations Processes

S. G. Thompson—ASSISTANT SECTION CHIEF
D. Gottlieb—SECRETARY

Group 1—Extraction-Decontamination

F. W. Albaugh—GROUP LEADER
M. Ader
L. S. Bartell
R. Bradt
C. Egan
R. W. Greenlee
H. R. Hoekstra
J. G. Malm
L. O. Morgan
S. Peterson
R. G. Post
J. Sedlet
R. C. Thompson

Group 2—Concentration-Isolation

D. G. Pye—GROUP LEADER
W. C. Beard, Jr.
R. H. Goeckermann
F. Haeckl
H. H. Hopkins, Jr.
J. J. Katz
A. E. Kelley
M. T. Walling
F. R. Yett

Group 3—Process Development

J. L. Dreher—GROUP LEADER
W. J. Blaedel
J. E. Freeman
J. R. Gilbreath
H. H. Hyman
R. G. Larson
D. C. Lincoln
A. Parnell
R. W. Rasmussen
B. M. Winner

Sub-Section II—Purification and Metal Production

E. F. Orlemann—ASSISTANT SECTION CHIEF
E. Kelly—SECRETARY

TABLE 1.4 (*Continued*)

Group 4—Purification and Analysis

L. H. Jensen—GROUP LEADER
B. B. Brody
J. S. Dixon
S. Lawroski
R. A. Reinhardt
A. P. Stein

Group 5—Volatility and General Dry Chemistry

N. R. Davidson—GROUP LEADER
B. M. Abraham
F. T. Hagemann
E. K. Hyde
I. Karle
I. Sheft
M. J. Wolf

Group 5a—Fluoride Chemistry

R. E. Heath—GROUP LEADER
A. E. Florin
F. Meyer
H. P. Zvolner

Group 6—Metal Production

H. L. Baumbach—GROUP LEADER
R. D. Frank
S. Fried
M. Gerstein
N. N. Hellman
Z. V. Jasaitis
J. Karle
S. Katz
H. P. Robinson
E. F. Westrum, Jr.

Group 6a—High Vacuum

O. C. Simpson—GROUP LEADER
N. D. Erway
L. Gilpatrick
F. Johnson
T. E. Phipps
G. W. Sears

Sub-Section III—Basic Chemistry and Service

B. B. Cunningham—ASSISTANT SECTION CHIEF
M. Bohlman—SECRETARY

Group 7—Basic Chemistry

J. C. Hindman—GROUP LEADER
D. P. Ames
J. J. Howland
R. A. James
K. A. Kraus
T. J. LaChapelle
C. K. McLane
L. B. Magnusson
P. R. O'Connor
C. Smith

Group 8—Recovery

L. R. Dawson—GROUP LEADER
H. H. Anderson
L. B. Asprey
N. S. Baumbach
J. W. Britain
J. G. Burr, Jr.
P. R. Fields
P. Fineman
L. Leventhal
D. C. Stewart
M. H. Studier
Q. Van Winkle

TABLE 1.4 (*Continued*)

Group 9—Instruments and Physical Measurements

A. Ghiorso—GROUP LEADER
J. A. Crawford
L. Golden
D. L. Hufford
A. H. Jaffey
T. P. Kohman
A. C. Krueger
B. F. Scott
P. D. Walsh
B. B. Weissbourd

TABLE 1.5 *Organization Chart of Section C-I, Metallurgical Laboratory (early 1945)*

G. T. Seaborg—SECTION CHIEF
E. Albaugh—SECRETARY TO SECTION CHIEF
W. M. Manning—ASSOCIATE SECTION CHIEF
J. Horwich—SECRETARY
T. O. Jones—ASSISTANT TO SECTION CHIEF
M. Williams—SECRETARY
K. Florin—SUPERVISOR OF SERVICE GROUP

Sub-Section I—Separations Processes

F. W. Albaugh—ASSISTANT SECTION CHIEF
D. Black—SECRETARY

Group 1—Extraction-Decontamination

R. C. Thompson—GROUP LEADER
R. Bradt
H. H. Hopkins, Jr.
J. G. Malm
L. O. Morgan
S. Peterson

Group 3—Process Development

J. R. Gilbreath—GROUP LEADER
M. Bolden—SECRETARY
W. C. Beard, Jr.
W. J. Blaedel
R. G. Post
J. Sedlet
M. T. Walling, Jr.
B. M. Winner

Group 4—Solvent Extraction

S. Lawroski—GROUP LEADER
C. J. Egan—SQUAD LEADER
I. J. Schaffner—ASST. SQUAD LEADER
B. Murray—TYPIST
M. Ader
G. J. Bernstein
B. B. Brody
D. J. Dorcy
E. A. Hausman
H. H. Hyman
A. E. Kelley
R. A. Reinhardt
J. H. Schraidt
W. Simon
B. Struminski

TABLE 1.5 (*Continued*)

Sub-Section II—Basic Chemistry and Service

B. B. Cunningham—ASSISTANT SECTION CHIEF
R. Rogers—SECRETARY

Group 5—Basic Dry Chemistry

O. C. Simpson—GROUP LEADER
N. R. Davidson—ASST. GROUP LEADER
B. M. Abraham
N. D. Erway
S. Fried
T. E. Phipps
H. P. Robinson
R. L. Seifert
I. Sheft
E. F. Westrum, Jr.

Group 6—Basic Wet Chemistry

J. C. Hindman—GROUP LEADER
D. P. Ames
J. S. Dixon
A. E. Florin
R. W. Greenlee
J. J. Howland
R. A. James
T. J. LaChapelle
L. B. Magnusson
C. K. McLane
P. R. O'Connor

Group 7—Recovery

D. C. Stewart—GROUP LEADER
H. H. Anderson
L. B. Asprey
J. W. Britain
P. R. Fields
P. Fineman
O. M. Giacchetti

Group 8—Instruments and Physical Measurements

A. Ghiorso—GROUP LEADER
A. H. Jaffey—ASST. GROUP LEADER
J. A. Crawford
J. M. Dorsey
D. L. Hufford
A. C. Krueger
E. Lewis
B. F. Scott
P. D. Walsh
B. B. Weissbourd

Group 9—U^{233} Work

L. I. Katzin—ASSISTANT SECTION CHIEF
F. T. Hagemann
N. N. Hellman
E. K. Hyde
R. G. Larson
M. H. Studier
Q. Van Winkle
M. J. Wolf

the very limited amounts of material with which they had to work and their lack of previous experience in very small-scale chemical manipulation.

The dry-chemistry program was organized roughly along the following lines: (1) studies of the preparation and properties of the

important classes of solid anhydrous plutonium compounds, such as oxides, halides, oxyhalides, sulfides, nitrides, etc.; (2) determination of the basic thermodynamics of such compounds; and (3) preparation and determination of the properties of plutonium metal. The very rapid progress achieved in carrying out the preparative portion of this program was due in large measure to two factors: the ingenuity and experimental skill displayed by the chemists in devising methods for conducting dry-chemical reactions in tiny, thin-walled capillary tubes, and the astonishing ability of W. H. Zachariasen in securing and interpreting X-ray diffraction patterns on products so prepared. Thus it was possible in many

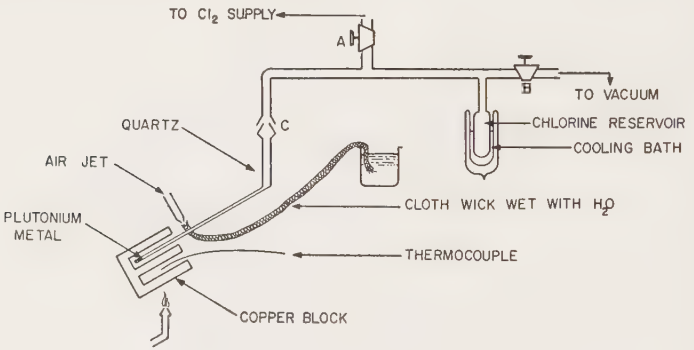


Fig. 1.7 Apparatus used to prepare the first sample of $PuCl_3$.

cases to determine the results of an experiment within a few hours *without destroying the sample*. Had it been necessary to depend upon conventional microanalysis for identification of compounds, days and even weeks might have been required for each analysis.

As an illustration of this technique, a description will be given of the first preparation and identification of the important compound $PuCl_3$. The compound was synthesized by F. T. Hagemann in February 1944. The apparatus used by Hagemann is illustrated in Fig. 1.7.

After a thorough preliminary heating and evacuation of the system to remove all water and oxygen adsorbed on the inner walls of the system, the quartz tubing, which was drawn down to a thin-wall capillary portion at the end, was disengaged at the standard taper joint "C" and a clean 50-microgram piece of metal was

introduced and shaken down to the tip of the capillary. The joint was then reconnected, sealed with vacuum wax, and evacuated through stopcock "B." "B" was then closed and "A" opened to a supply of pure chlorine gas. A small amount of liquid chlorine was condensed in a glass reservoir cooled with a mixture of solid carbon dioxide and acetone, as shown in Fig. 1.7. Upon closing "A" the system remained filled with chlorine gas at a pressure of about 60 millimeters, the pressure of chlorine gas in equilibrium with liquid chlorine at the freezing bath temperature.

The copper block was heated to 45°C and the temperature maintained for fifteen minutes, after which all chlorine was removed from the system by pumping through stopcock "B." After an additional 10 minutes of heating at 450°C, with "B" open to the pumping system, the cooled section of capillary just beyond the heating block was examined for a sublimate, which would have indicated the formation of a plutonium chloride of relatively high volatility. No sublimate was observed, however. After removal of the furnace, a blue reaction product could be observed in the top of the capillary. The section of the capillary containing the product was sealed off and submitted to W. H. Zachariasen for X-ray examination. From the diffraction pattern obtained, Zachariasen was able to state that the preparation consisted of a single phase, which was hexagonal and isostructural with UCl_3. The identity of the product as $PuCl_3$ was thus quickly established in an unequivocal way.

By similar methods Hagemann prepared PuI_3 and a mixed plutonium tribromide-trichloride, which were identified by Zachariasen from their X-ray diffraction patterns. The preparation of pure plutonium tribromide was achieved first by E. K. Hyde, and its identity was established by conventional chemical analysis. At a later date, S. Fried and N. R. Davidson made very effective use of the capillary preparative technique described above to produce the first pure neptunium halides; they also produced the first neptunium metal by the reduction of neptunium trifluoride with barium.

Quite often in working with very small amounts of material the products obtained were prepared inadvertently, due to the presence of impurities (especially traces of water and oxygen), and

in such cases the X-ray diffraction method quickly revealed the true situation. It was in this way, for example, that plutonium oxyiodide was first obtained and identified.

In the early work on the preparation and identification of the plutonium fluorides A. E. Florin and R. E. Heath were the principal contributors, although the fluoride research later expanded to include many investigators, among whom were J. Karle, C. S. Smith, H. H. Anderson, Davidson, and Fried; L. B. Magnusson and T. J. LaChapelle did much of the work on neptunium fluorides. Work on the chloride, bromide, and iodide of plutonium was carried on by Davidson, J. J. Katz, E. K. Hyde, F. T. Hagemann, B. M. Abraham, B. B. Brody, I. Karle, M. J. Wolf, and I. Sheft.

E. F. Westrum, Jr., made important investigations of the oxides, PuO_2, Pu_2O_3, and PuO, while studies of the sulfides, oxysulfides, and nitrides were conducted by Abraham, Davidson, and Westrum.

In pursuing the second objective of research in the dry chemistry program—that of securing basic thermodynamic data on these substances—three general lines of approach were used: (1) direct thermochemical measurements, (2) observations of the temperature coefficient of equilibrium constants, and (3) rough estimates of lower or upper limits of stability by noting the presence or absence of reactions under chosen experimental conditions.

The success of the thermochemical program was due in very large measure to the efforts of Westrum and H. P. Robinson, who succeeded in constructing a heat-of-solution calorimeter of semimicro size and high accuracy. With this apparatus Westrum and Robinson determined standard heats of formation of plutonium aqueous ions, and from these, of solid plutonium trifluoride, trichloride, tribromide, and oxychloride, using milligram samples.

Notable contributions to the plutonium thermodynamics program were made by Davidson, Sheft, and Fried, who investigated various halide and oxyhalide equilibria as a function of temperature. A special contribution to plutonium compound thermodynamics was that of O. C. Simpson, T. E. Phipps, G. W. Sears, and R. L. Seifert, who carried out a series of remarkably precise measurements of the vapor pressures of PuF_3, $PuCl_3$, and $PuBr_3$ as a function of temperature and also investigated the volatility of plutonium oxide at elevated temperatures.

In all of the work on plutonium thermodynamics done at Chicago, much benefit was derived from correspondence and occasional consultation with L. Brewer of the University of California, whose extensive knowledge of, and insight into, the field of thermodynamics served to clarify and, in some cases, to correct initial conclusions concerning the experimental data.

The third and perhaps most exciting phase of the early program on plutonium dry chemistry was that which had as its objective the preparation and determination of certain physical properties of plutonium metal, pertinent to its use in a nuclear weapon.

Following some unsuccessful attempts to make elemental pluto-

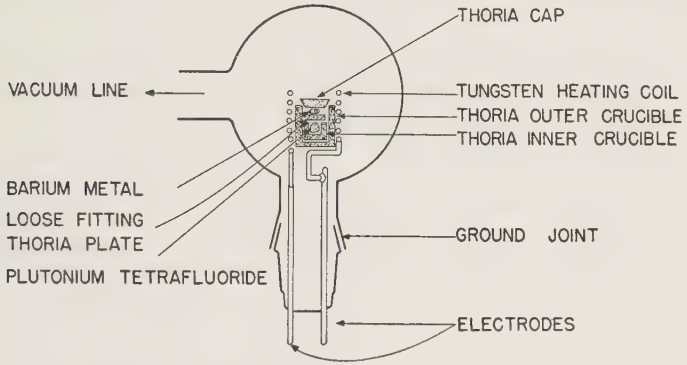


Fig. 1.8 Apparatus used to prepare the first sample of plutonium metal.

nium by reacting the oxide with metallic potassium, H. L. Baumbach and P. L. Kirk in November 1943 made the first microgram samples of the metal by reducing 35 micrograms of plutonium tetrafluoride with metallic barium in a thoria crucible at 1400°C, using the apparatus depicted in Fig. 1.8. The metal appeared in globules weighing about 3 micrograms each, and it had a silvery luster. It was proved to be the metal by the fact that it reacted rapidly with hydrogen to form plutonium hydride.

The crucible assembly and heating coil were inserted into a high vacuum system, and after preliminary outgassing of the crucible assembly in high vacuum at high temperature, the assembly was removed to an inert atmosphere and the inner crucible was charged with a few micrograms of plutonium tetrafluoride. The spacer was then dropped into place and a piece of metallic barium

placed on top of it. After wedging the thoria cap tightly into place, the crucible assembly was inserted into the heating coil and the whole replaced in the vacuum system. When a good vacuum had been attained once more, current was passed through the heating coil, thus raising the crucible temperature to around 1400°C. Barium vapor then reacted with the plutonium tetrafluoride to produce barium fluoride and plutonium metal. Excess barium escaped through the pores of the thoria crucible. When all excess barium had been removed, the crucible was allowed to cool and was then opened for recovery of plutonium. The metal, drained free of barium fluoride slag, which soaked into the thoria, appeared as tiny globules of bright metal, adhering to the wall of the inner crucible.

Using metal produced in such a system, Kirk and Baumbach, later joined by Fried, determined the density of their samples by dropping a weighed piece into a capillary tube of known diameter, partially filled with dibutylphthalate, an inert organic liquid of low vapor pressure. From the displacement of the liquid meniscus caused by adding the metal, the volume of the piece could be determined, and, from this volume and the known weight of the sample, the density of the earliest samples was calculated to be 16 grams per cubic centimeter. The density so determined (probably not that of a single pure phase of the metal) was later confirmed by W. H. Zachariasen by X-ray diffraction measurements. Using such metal Z. V. Jasaitis was able to determine the melting point, and R. S. Rosenfels developed methods for mounting the metal for hardness determinations and metallographic examination.

The ultramicroscale method of metal production described above was modified and improved by Fried and Westrum, who made major contributions to the program on metallic plutonium.

Later, at the time milligram amounts of plutonium became available for research, O. C. Simpson and his colleagues were able to get very precise measurements of the vapor pressure of the liquid metal over an extended range of temperature.

Worthy of special mention is the work of J. C. Hindman and co-workers on the solution chemistry of plutonium. They made many fundamental contributions to the elucidation of the ionic species present in aqueous solutions of different acids and to the determination of various complex ions of plutonium. K. A. Kraus

also made many important contributions to these general problems. The over-all contributions of B. B. Cunningham to this solution-chemistry program, as well as to the above mentioned dry-chemistry program, were noteworthy.

The problem of the purification of the plutonium to the stringent specifications required for its use as a weapon was, as mentioned above, the responsibility of E. F. Orlemann. Under his excellent direction many results, useful to the Los Alamos chemistry group in helping them meet their requirements, were obtained. Of especial importance was the work of Orlemann's group in developing various solvent extraction procedures for this purpose. Important contributions to the program were made by L. H. Jensen, J. I. Watters, B. B. Brody, R. A. Reinhardt, J. S. Dixon, and others. The development of analytical methods of importance to this program was done in a group under the leadership of H. A. Potratz. M. S. Fred and N. H. Nachtrieb made valuable contributions to spectrographic analysis methods.

Also very important to the effort of the chemistry groups at the Metallurgical Laboratory was the work of the "Recovery Group," under the direction of L. R. Dawson and later under D. C. Stewart. This group had the important assignment of continuously recovering for reuse the precious plutonium as it found its way into peculiar places in the course of the experimentation program.

Problems on instrumentation and radioactivity measurements were in the capable hands of A. Ghiorso, A. H. Jaffey, T. P. Kohman, C. J. Borkowski and H. P. Robinson, with the help of J. A. Crawford, D. L. Hufford, B. B. Weissbourd, B. F. Scott, and others.

Important research on the Bismuth Phosphate Process was continued at the Metallurgical Laboratory, with particular emphasis on the Hanford problem after the Clinton plant went into operation. The Process was successfully tested at the Hanford concentration of plutonium on the liter scale of operation in stainless-steel equipment in the experiments of J. R. Gilbreath, H. R. Hoekstra, and co-workers. In addition, a semi-works program of investigation was carried on by a group under the leadership at various times of C. J. Egan and J. L. Dreher. It was particularly evident that a special study of the Hanford concentration and isolation procedures

was needed because of the great difference in this phase of the process between the Clinton and Hanford operations. A group was established under G. W. Watt in October 1943 to study the isolation step, i.e. the final precipitation of plutonium without the benefit of carrier. As mentioned earlier, the short time schedule forced the choice of the compound to be precipitated here before sufficient data had been obtained to assure success for the procedure. The precipitation of the peroxide from the lanthanum-containing solution obtained in the concentration step was the choice, and the careful research of this group led to successful solutions for the numerous difficult problems that presented themselves. Many of the people working on the extraction process, both at the Metallurgical Laboratory and the Clinton Laboratories, transferred to Hanford when that plant neared the date for beginning operation. Both of these laboratories served as training ground for many of the duPont personnel who took part in the operation of the plant and the supporting research at Hanford.

1.10b University of California

The group remaining at the University of California under the over-all direction of W. M. Latimer, after the removal of J. W. Kennedy, A. C. Wahl, M. L. Perlman, C. S. Garner, R. J. Prestwood, D. Lipkin, S. I. Weissmann, R. B. Duffield, and others to Los Alamos in the spring of 1943, continued to make important contributions. R. E. Connick and a group consisting of W. H. McVey, G. E. Sheline, J. W. Hamaker, M. Kasha, M. W. Evans, E. L. King, and others made outstanding advances in the solution chemistry of plutonium, including the oxidation states and potentials and reaction kinetics. E. D. Eastman, L. Brewer, and a group consisting of L. A. Bromley, D. D. Cubicciotti, Jr., N. L. Lofgren, C. D. Thurmond, O. A. Cook, B. J. Fontana, M. J. Sienko, P. W. Gilles, and others contributed notably to the important problem of finding suitable container material in which to carry out the reduction of plutonium fluoride to the metallic state, which was of crucial importance to the success of the Los Alamos task. G. K. Rollefson and H. W. Dodgen were the first to determine a number of the important lines in the plutonium emission spectrum. R. Overstreet and L. O. Jacobson, with J. G. Hamilton, worked on the identification of a number of fission products.

J. W. Gofman and a group consisting of H. W. Crandall, G. C. Pimentel, W. H. Reas, and C. E. Crompton made contributions to the plutonium extraction and decontamination problem. They worked out a process in which plutonium (IV) could be coprecipitated with thorium oxalate under conditions where the bulk of the uranium remained in solution as a complex ion; the initial extraction was followed by reprecipitations and other steps to effect the ultimate decontamination from fission products which was required.

It might also be mentioned that before Wahl went to Los Alamos, he and a group working with him worked out on the laboratory scale another extraction process, the "Acetate Process," for the separation and decontamination of plutonium. In this process plutonium (VI) is coprecipitated with sodium uranyl acetate, which is redissolved and, after reduction of the plutonium to the IV state, is reprecipitated, leaving the plutonium in solution. Decontamination from the fission products is effected by repeating this cycle with less uranium carrier. This process was under serious consideration for adoption and use at Hanford, but it had the crucial disadvantage that the entire bulk of uranium had to be handled as a precipitate. However, it was used successfully during the summer and fall of 1943 for isolation of several milligrams of plutonium from about a half ton of cyclotron-neutron-irradiated uranium. The group at Berkeley with Gofman put the material through the initial chemical cycles which reduced the amount of uranium associated with the plutonium to about a pound and eliminated the fission products. At Los Alamos, Wahl, Duffield, Garner, and Prestwood continued the purification until pure plutonium compounds were precipitated. This plutonium was of great value in the development of the process used to purify plutonium to the stringent specifications necessary for use in the weapon.

1.10c Iowa State College

F. H. Spedding, together with A. F. Voigt and F. J. Wolter at Iowa State College, contributed to the chemistry of complex-ion formation as well as to other phases of plutonium chemistry. A number of important contributions to the study of the fission products were made by W. H Sullivan, A. S. Newton, and their coworkers, while J. C. Warf and his group made important analytical

chemical contributions. I. B. Johns, Jr., H. A. Wilhelm, and the group at Iowa State worked on pyrometallurgical methods for the extraction of plutonium from uranium and for its decontamination from the fission products. Interesting methods which depended on extraction with liquid metals and volatilization from molten uranium at high temperatures were investigated, and these were the forerunners of the important research being carried on today on this approach to the problem. Many are of the opinion that a method of this type will be the best ultimate method because it is not necessary to put the uranium or plutonium into aqueous solution, thus simplifying or even avoiding the costly step of reduction to the metal.

1.10d Redox Process

Since the Bismuth Phosphate Process did not recover the uranium for reuse, a program to find a more suitable separation process for long-range use was initiated at the Metallurgical Laboratory in 1944. Early that year I conceived of the principle of alternating between the plutonium (III) oxidation state and a higher oxidation state or states as the basis for separating plutonium from uranium and decontaminating it from fission products by the use of organic solvents. The first application of this principle, now widely used, was in the "Redox Process," developed at the Metallurgical Laboratory beginning in 1944 and, on the basis of much additional work there and at other sites, put into operation by the scientists and engineers of the General Electric Company at Hanford in 1951. Among the pioneer workers were W. J. Blaedel, who had the faith and perseverance necessary to override the initial difficulties, and H. H. Hyman, S. Lawroski, I. J. Schaffner, and L. R. Dawson, all of whom received much important support and encouragement from T. R. Hogness, in the face of great Manhattan District official resistance to the development of such a much-needed substitute process. In fact, this important and rather large-scale effort was carried on by our group as essentially "bootleg research" during much of 1945. J. O. Maloney, J. B. Tepe and co-workers also carried on early investigations on the semi-works scale. The Redox Process comprises a number of cycles in the course of which the required separations are effected. The first cycle consists of three

columns in which plutonium and uranium are separated from each other and the bulk of the fission products. The feed solution is a uranyl-nitrate solution containing a minimal amount of nitric acid and heavily salted with aluminum nitrate. Oxidation with sodium dichromate converts plutonium to the solvent-extractable (VI) state, and both the uranium and plutonium are extracted into hexone. The organic phase is scrubbed in the same column with aluminum-nitrate solution to remove fission products. In a second column, the plutonium is stripped from the organic phase by reducing the plutonium to the nonextractable (III) state, with a reducing agent (ferrous sulfamate) which does not affect the uranium. In the third column, the uranium is stripped from the hexone with dilute nitric acid. The plutonium recovered from the first cycle is further decontaminated by additional solvent extraction cycles. The uranium product from the first cycle is evaporated and likewise subjected to a second and third solvent extraction cycle to yield uranium essentially free of fission products or plutonium, suitable for return to an isotope enrichment plant or to a nuclear reactor.

1.10e TTA Process

Another interesting solvent extraction process for separating and decontaminating plutonium was developed at the University of California near the end and just after the end of the war. This procedure was conceived by M. Calvin and developed with the help of J. C. Reid, H. W. Crandall, J. F. Thomas, E. L. Zebroski, and co-workers with later contributions on an engineering scale by T. Vermeulen, T. E. Hicks, M. W. Davis, Jr., B. Rubin, and associates. In this process, plutonium (IV) is extracted from the aqueous feed with a benzene-thenoyltrifluoracetone (TTA) solution, leaving uranium and essentially all fission products except zirconium. Traces of fission products are scrubbed from the organic phase with dilute nitric acid. Plutonium is then stripped from the organic phase by scrubbing with a reducing agent. Plutonium (III) is not extracted by TTA to a significant extent; thus the plutonium is transferred to the aqueous phase. The plutonium is decontaminated from zirconium by this procedure, since zirconium is not stripped from the benzene layer. Zirconium is then removed from the solvent by an oxalic-nitric acid scrub, after which the benzene-TTA is

ready for reuse. Uranium is recovered and further decontaminated by solvent extraction with TTA-hexone. This process, in comparison to other solvent extraction methods which do not employ chelating agents, has the not inconsiderable advantage that no metal salting-agents are employed, thus reducing waste disposal problems. A significant disadvantage, however, is that the rate of chelation is slow, which of course has rather serious consequences for a continuous operation.

1.10f Chalk River Laboratory

Any account of other contributors to the wartime work on plutonium should not end without a description of the excellent research that took place at the Chalk River Laboratory in Canada.

Research in Britain began at a very early date and centered mainly in the Cavendish Laboratory at Cambridge University. Production of uranium metal and uranium hexafluoride was undertaken by Imperial Chemical Industries in the Liverpool area in 1941.

Because of the danger from enemy action, and also in an attempt to integrate the British and American efforts, the British research effort was moved in 1943 to a new laboratory in Montreal, where the staff was augmented by many Canadian scientists. The project was under the joint control of the British Ministry of Supply and the Canadian National Research Council. Some members of the British research team joined laboratories in the United States, but collaboration was never very close.

The Montreal laboratory was under the direction first of H. von Halban and later of J. D. Cockcroft. E. W. R. Steacie of the Canadian National Research Council was deputy director. L. Kowarski also was a key figure in the operation of the Laboratory. The chemistry group, under the direction first of F. A. Paneth and later of J. Guéron and B. Goldschmidt, made studies of plutonium chemistry and of separation methods suitable for large-scale operation.

The chemical properties of plutonium were studied by H. G. Heal, A. G. Maddock, and B. G. Harvey, including investigation of oxidation and reduction reactions between the III, IV, and VI states. Many compounds of plutonium in these states were prepared. A survey was made of the reactions of Pu^{+3} and Pu^{+4} with

a large number of organic complexing reagents. A second group under the direction of B. Goldschmidt studied methods for the large-scale extraction of plutonium from uranium fuel elements. L. G. Cook and R. W. Spence, who later became directors of the chemistry groups at Chalk River and Harwell respectively, were members of Goldschmidt's group. Many organic solvents were tested for suitability. The process which was finally chosen was based on the preferential extraction of Pu^{+4} from aqueous ammonium nitrate solutions by the solvent triglycoldichloride, known as the "Trigly Process." A plant using this process was later built at Chalk River and operated successfully.

In 1944 a large part of the Canadian effort was moved to a new permanent site at Chalk River, Ontario, about 120 miles west of Ottawa on the Ottawa River. A little later, the British group began to move back to its permanent headquarters at Harwell, near Oxford. J. D. Cockcroft went to Harwell as director, and W. B. Lewis took over scientific direction of the Chalk River effort.

1.11 Properties of Plutonium

The successful operation of the reactor and plutonium extraction plant at Oak Ridge, Tennessee led to the availability of first milligram, and then gram, amounts of plutonium early in 1944. The availability of milligram amounts of plutonium led to the immediate discovery of the III oxidation state. The early tracer work at the University of California in 1941 had established the existence of a lower oxidation state (IV and/or III state) and a higher state (VI and/or higher state); and the ultramicrochemical work late in 1942 and early in 1943, as mentioned above, had defined the existence of the IV and VI states. The III oxidation state was discovered early in 1944 by R. E. Connick, W. H. McVey and G. E. Sheline (who actually worked with about 0.25 milligram of cyclotron-produced plutonium) at the University of California and, essentially simultaneously, by J. C. Hindman, K. A. Kraus, J. J. Howland, Jr., and B. B. Cunningham at the Metallurgical Laboratory and D. F. Mastick and A. C. Wahl at the Los Alamos Laboratory; the latter two groups utilized the milligram amounts of plutonium made available at that time through the operation

of the reactor and chemical separation plant at the Clinton Laboratories. The existence of the V oxidation state was established in the summer of 1944, through the use of plutonium obtained from the Clinton Laboratories, by Connick, M. Kasha, McVey and Sheline.

The production early in 1945 of larger amounts came as a result of operation of the Hanford plant. Continuing investigations of the chemical properties of plutonium in many laboratories throughout the world, as it has become available, has led to the situation where the chemistry of this relative newcomer is as well understood as is that of most of the well-studied elements. Thus, plutonium has the four oxidation states—III, IV, V, and VI—leading to a chemistry which is as complex as that of any other element. In fact, it is unique among the elements in that these four oxidation states can all exist simultaneously in aqueous solution at appreciable concentration (see below, Chapter 2). As a metal, too, its properties are unique. It has six allotropic forms (see below, Table 2.2), in the temperature range from room temperature to its melting point (640°C), and some of these have properties not found in any other known metal. Much about the chemical properties of plutonium will be found in Chapter 2.

The nuclear properties of the isotopes of plutonium are also very interesting. All of the isotopes from Pu^{232} to Pu^{246} are known, and their radioactive properties are summarized in the Appendix, below. In addition to Pu^{238} and Pu^{239} the wartime discoveries were Pu^{241} (by R. A. James, L. O. Morgan, A. Ghiorso, and myself), Pu^{240} (by O. Chamberlain, G. W. Farwell, and E. Segrè), Pu^{237} and Pu^{236} (by James, A. E. Florin, H. H. Hopkins, Jr., and Ghiorso), and Pu^{234} (by E. K. Hyde, M. H. Studier, and Ghiorso). The Pu^{241} was produced by neutron bombardment of Pu^{239} at the Clinton Laboratories and identified at the Metallurgical Laboratory; the Pu^{240} was similarly produced and identified at the Los Alamos Laboratory through its spontaneous fission, while the others were produced in charged-particle bombardments with the Berkeley 60-inch cyclotron and identified at the Metallurgical Laboratory. The lighter isotopes may, in general, be produced by charged-particle bombardments, while the isotopes Pu^{239} and above (and also Pu^{238}) can be produced in quantity by neutron bombardment.

Many future investigations of the chemical and physical properties of plutonium may be made using the isotope Pu^{242}, rather than Pu^{239}, because of the longer half life of the former, making the difficulties associated with investigations involving a radioactive substance less serious. The isotope Pu^{244} (half life, 7.6×10^7 years) is especially interesting because of its long half life, and offers intriguing possibilities for the more distant future. The fission and neutron-absorption properties of many of the isotopes of plutonium are known. Of key importance, of course, are the fission properties of Pu^{239}. Much about the nuclear properties of plutonium isotopes will be found in Chapter 3, below.

It is beyond the scope of the present account to discuss the properties of plutonium which make it useful as the explosive ingredient of a nuclear weapon. Plutonium, fortunately, has, in addition to this use, very important application in industrial nuclear power. Nuclear reactors may be built to use the isotope Pu^{239} as fuel. Such reactors can operate as "breeders" in conjunction with the abundant uranium isotope, U^{238}; such a system "burns" U^{238} indirectly through the medium of fissionable Pu^{239} formed by the absorption of neutrons in U^{238}. A fissionable isotope such as Pu^{239} gives rise to an amount of heat energy equivalent to approximately 10,000,000 kilowatt hours per pound when it completely undergoes the fission reaction. In industrial uses the energy may be used in this heat form or, in most cases, converted into the more convenient electrical form by more or less standard turbine equipment.

Included among its unusual properties is the extremely poisonous character of plutonium (Pu^{239}); in point of fact, it is one of the most dangerous poisons known to man, as a result of its alpha radioactivity and chemical properties, which cause it to find a more or less permanent site in the bone after assimilation. Much of our knowledge of the physiological behavior of plutonium was derived from the animal studies of J. G. Hamilton and his associates at the University of California Crocker Radiation Laboratory. Special equipment and precautions are necessary in the investigations of its properties, and continued use of milligram amounts for such experiments is advisable even though larger amounts might be available. Even if there were no other reasons, its high alpha radioactivity places it, especially in the form of Pu^{239}, outside the class of

elements that might eventually find widespread use among chemists for investigation of its chemical properties. The use of the longer-lived isotope Pu^{242} mitigates these difficulties to some extent.

1.12 Isolation of Neptunium

Nearly as interesting as the story of the first isolation of pure plutonium is that of pure neptunium, the second synthetic element to be isolated in pure form. The early chemistry of neptunium, like that of plutonium (for which Pu^{238} was used), was limited to studies by the tracer technique using the short-lived isotope, Np^{239}. Fortunately, there is another isotope of neptunium, Np^{237}, which was discovered early in 1942 by A. C. Wahl and the author at the University of California, and which is sufficiently long-lived to make work with weighable amounts possible. This isotope is the decay product of the previously known seven-day, beta-particle emitter, U^{237}, which is formed as the result of an $(n, 2n)$ reaction of U^{238}, and is an alpha emitter of relatively long half life, 2.20×10^6 years.

The first weighable amounts of Np^{237} were produced by the bombardment of large amounts of uranium with the fast neutrons from the cyclotron. The reaction for the production of this isotope is such that the yield is considerably less than that for Pu^{239}, and, therefore, the total amounts available for early work on neptunium were even smaller than the tiny amounts of Pu^{239} referred to above. Nevertheless, L. B. Magnusson and T. J. LaChapelle, working with J. C. Hindman at the Metallurgical Laboratory of the University of Chicago, were able, during 1944, to isolate the element in the form of pure compounds and to study a number of its important chemical properties. The equipment and techniques were the same as those described above. A picture of the first neptunium, 10 micrograms of the oxide (NpO_2), isolated in July 1944, is shown in Fig. 1.9. Larger amounts of this isotope were later available. It is very fortunate, indeed, that the large chain-reacting units produce this isotope, and that by means of special chemical extraction procedures it has been possible to extract and make it available for chemical studies (see below, Section 1.15d). Using such material, it has been possible to make an intensive study of the chemical properties of neptunium, leading to a thorough understanding of its chemical properties.

Fig. 1.9 First neptunium compound (ten micrograms of oxide) at bottom of capillary tube (magnified about 20-fold) isolated in July 1944. Below the sample, for purposes of comparison, is a millimeter scale, and above the sample a U. S. 10-cent piece (dime).

1.13 Plutonium and Neptunium in Nature

It is interesting to note that both plutonium (Pu^{239}) and neptunium (Np^{237}) exist in nature in very small concentrations in uranium-containing ores. These isotopes are formed continuously as the result of the interaction of neutrons with U^{238}. The neutrons are those emitted during the spontaneous fission of uranium and the slow neutron fission of U^{235}, and those resulting from the action of alpha particles on the nearby light elements. The concentrations are determined in each case by the equilibrium balance between the rate of formation and the rate of radioactive decay. The concentration also depends on the amount of neutron-absorbing impurities in the ore.

Early in 1942 M. L. Perlman, working with me in Berkeley, undertook a search for plutonium in pitchblende, the primary purpose at that time being to establish whether such a source of a fissionable transuranium isotope might substitute for the, at that time, undeveloped and questionable nuclear chain reaction for production purposes. Although the experiment proved that this could not be a practical source for the production of plutonium, an amount of plutonium corresponding to about one part in 10^{12} was found in the pitchblende. This concentration is approximately that to be expected on the basis of the absorption of the available neutrons by the uranium in the ore. Work in the summer of 1942 by C. S. Garner and N. A. Bonner in Berkeley established the presence of plutonium in carnotite. D. F. Peppard, M. H. Studier, M. V. Gergel, G. W. Mason, J. C. Sullivan, and F. Mech of the Argonne National Laboratory have extracted microgram quantities of plutonium from pitchblende-processing solutions corresponding to ore concentrations similar to those mentioned above, and Peppard, Mason, P. R. Gray, and Mech have established the presence of similar, although somewhat smaller, concentrations of Np^{237}, also formed by the action of neutrons on the uranium. A more complete investigation of the presence of plutonium in various uranium ores has been made by C. A. Levine and the author, with the results shown in Table 1.6. The lower concentrations (actually limits of concentration) in fergusonite and carnotite are due to the presence of neutron absorbing substances.

Table 1.6 *Concentration of Plutonium in Uranium Ores*

	U, %	$Pu^{239}/U \times 10^{12}$
Canadian pitchblende	13.5	7.1
Belgian Congo pitchblende	38	12
Colorado pitchblende	50	7.7
Brazilian monazite	0.24	8.3
North Carolina monazite	1.64	3.6
Colorado fergusonite	0.25	<4
Colorado carnotite	10	<0.4

1.14 Americium and Curium

After the completion at the wartime Metallurgical Laboratory of the most essential part of the investigations concerned with the chemical processes involved in the production of plutonium, our attention turned to the problem of synthesizing and identifying the next transuranium elements. As collaborators in this endeavor, there were A. Ghiorso, trained in electrical engineering, who played a dominant role in the development of the electronic instruments used in our radioactivity investigations, and two young chemists, R. A. James and L. O. Morgan, who had been especially proficient in the investigations involving the chemistry of the transuranium elements.

There followed a period during which the attempts to synthesize and identify elements 95 and 96 bore no fruit. The unsuccessful experiments were based on the premise that these elements should be much like plutonium, in that it should be possible to oxidize them to the VI oxidation state and utilize this oxidation in the chemical isolation procedures. It was not until the middle of the summer of 1944, upon the first recognition that these elements were part of an actinide transition series (discussed further in the next chapter) that any advance was made; and then progress came quickly.

As soon as it was recognized that the elements could be oxidized above the III state only with extreme difficulty, if at all, the identification of an isotope then thought to be due to element 96 or 95 followed immediately. Thus the isotope now known to be Cm^{242} was produced in the summer of 1944 as a result of the bombardment

of Pu^{239} with 32-Mev helium ions. The reaction involved is $Pu^{239}(\alpha,n)Cm^{242}$. The bombardment took place in the Berkeley 60-inch cyclotron, after which the material was shipped to the Metallurgical Laboratory for chemical identification.

Since the original short account of this discovery (published at the time only in a secret Metallurgical Laboratory progress report) has never been made generally available, I reproduce it here, verbatim, from the report (CS-2135), covering the period of August 1944:

About 10 mg of Pu^{239} were bombarded to the extent of 40 μahr with 32 Mev helium ions in the Berkeley sixty-inch cyclotron. There was found in this material a new radioactivity, emitting alpha-particles of range about 4.7 cm, which seems to be due to an isotope of element 96 or 95. This new radioactivity is carried quantitatively by lanthanum fluoride, even in the presence of oxidizing agents such as dichromate or silver persulfate, indicating that this isotope cannot be oxidized to a +6 oxidation state in aqueous solution. The activity is carried by lanthanum oxalate in the presence of excess alkaline oxalate and not carried from acid solution by zirconium phenylarsonate, lead sulfate, or bismuth phosphate.

The identification of element 95 followed, late in 1944, as a result of the bombardment of Pu^{239} with pile neutrons, the production reactions being as follows:

$$Pu^{239} + n \rightarrow Pu^{240} + \gamma$$
$$Pu^{240} + n \rightarrow Pu^{241} + \gamma$$
$$_{94}Pu^{241} \xrightarrow{\beta^-} {}_{95}Am^{241}.$$

At the same time the isotope Cm^{242} is formed as follows by the method which is also presently the best for its production:

$$Am^{241} + n \xrightarrow{\beta^-} Am^{242} + \gamma$$
$$_{95}Am^{242} \xrightarrow{\beta^-} {}_{96}Cm^{242}.$$

Again, a verbatim quotation from the original Metallurgical Laboratory Report, CS-2741, for the month of February 1945, seems appropriate:

Some very interesting new alpha-radioactivity has been found, both in plutonium irradiated with neutrons in the Clinton pile and plutonium irradiated with neutrons in the Hanford pile. This alpha-activity exhibits just the sort of chemical behavior which has been predicted for the trans-

plutonium elements. For example, it is carried by rare earth fluorides and it has not yet been possible to oxidize it to a state or states where its fluoride is soluble. It seems to be chemically separable from all the rest of the 94 elements, and the best present interpretation is that it is due to elements 95 and/or 96. The alpha-activity is composed of two components, one of range 4.0 cm and the other of range 4.7 cm. A very attractive possibility is that the 4.0 cm alpha-activity corresponds to 95^{241} formed from the beta-decay of 94^{241} which comes from the reaction $94^{240}(n,\gamma)94^{241}$, and the 4.7 cm alpha-activity corresponds to 96^{242} (cf. reports CS-2124 and CS-2135) from beta-decaying 95^{242} following the reaction $95^{241}(n,\gamma)95^{242}$. The ratio of the yields in the Hanford as compared to the Clinton bombardment seems to be proportional to the second power of the total neutron irradiation, as would be expected on the basis of these particular isotopic assignments, although the accuracy of the estimation of the neutron fluxes is not sufficient to make this at all certain.

Some comments should be made here concerning the rare-earth-like properties of these two elements. Our hypothesis that they should have a stable III oxidation state and greatly resemble the rare earth elements in their chemical properties proved to be so very true that for a time it appeared to be unfortunate. The better part of a year was spent in trying, without success, to separate chemically the two elements from each other and from the rare earth elements, and although we felt entirely confident, on the basis of their radioactive properties and the methods of production, that isotopes of elements 95 and 96 had been produced, the chemical proof was still undemonstrated. The elements remained unnamed during this period of futile attempt at separation (although one of our group referred to them as "pandemonium" and "delirium," in recognition of our difficulties). However, they were finally separated and completely identified chemically, and their present names were eventually proposed on the basis of their chemical properties. The name "americium" (symbol Am) was suggested for element 95, thus calling it after the Americas, by analogy with the naming of its rare earth homologue, europium, after Europe; and the name "curium" (symbol Cm) was suggested for element 96, after Pierre and Marie Curie, by analogy with the naming of its homologue, gadolinium, after J. Gadolin.

It is interesting to note that the discovery of these elements was informally revealed on a nationally broadcast radio program, the

Quiz Kids, on which I appeared as a guest on November 11, 1945. This information had been declassified for presentation at an American Chemical Society symposium at Northwestern University in Chicago the following Friday, at which place and time the discovery was more formally announced. Therefore when one of the youngsters asked me, during a session in which I was trying to answer their questions, if any additional new elements had been discovered in the course of the research on the nuclear weapon during the war, I revealed the existence of the elements 95 and 96. Apparently many children in America told their teachers about it the next day and, judging from some of the letters which I subsequently received from such youngsters, they were not entirely successful in convincing their teachers.

Americium was first isolated by B. B. Cunningham in the form of a pure compound, the hydroxide, in the fall of 1945 at the wartime Metallurgical Laboratory; a photograph of his hydroxide is shown in Fig. 1.10. It can be prepared in gram and larger amounts by the neutron bombardment of plutonium according to the reactions shown above, and it has thus been possible to investigate its chemical properties through the use of macroscopic quantities.

Curium was first isolated in the form of a pure compound, the hydroxide, of Cm^{242} by L. B. Werner and I. Perlman at the University of California during the fall of 1947. A photograph of this first hydroxide is shown in Fig. 1.11. The isotope Cm^{242} is so highly radioactive, because of its short half life, that chemical investigations with it in macroscopic concentrations are very difficult. Nevertheless, a number of such investigations have been carried on, and much has been learned about its chemical properties.

Fortunately, longer-lived isotopes of americium and curium are now available for use in the investigation of the chemical properties of these elements. Thus we have Am^{243} (half life, 7,950 years) and Cm^{244} (half life, 19 years), as well as heavier isotopes of curium which have even longer half lives. This availability is particularly important in the case of curium, because of the difficulties of working with the short-lived Cm^{242}. The methods of production for these heavier isotopes are described in Chapter 3, below.

Fig. 1.10 First photograph of an americium compound. The hydroxide is shown in the bottom of the tube (center). Americium was first isolated in the fall of 1945. Eye of sewing needle below indicates magnification of about 15-fold.

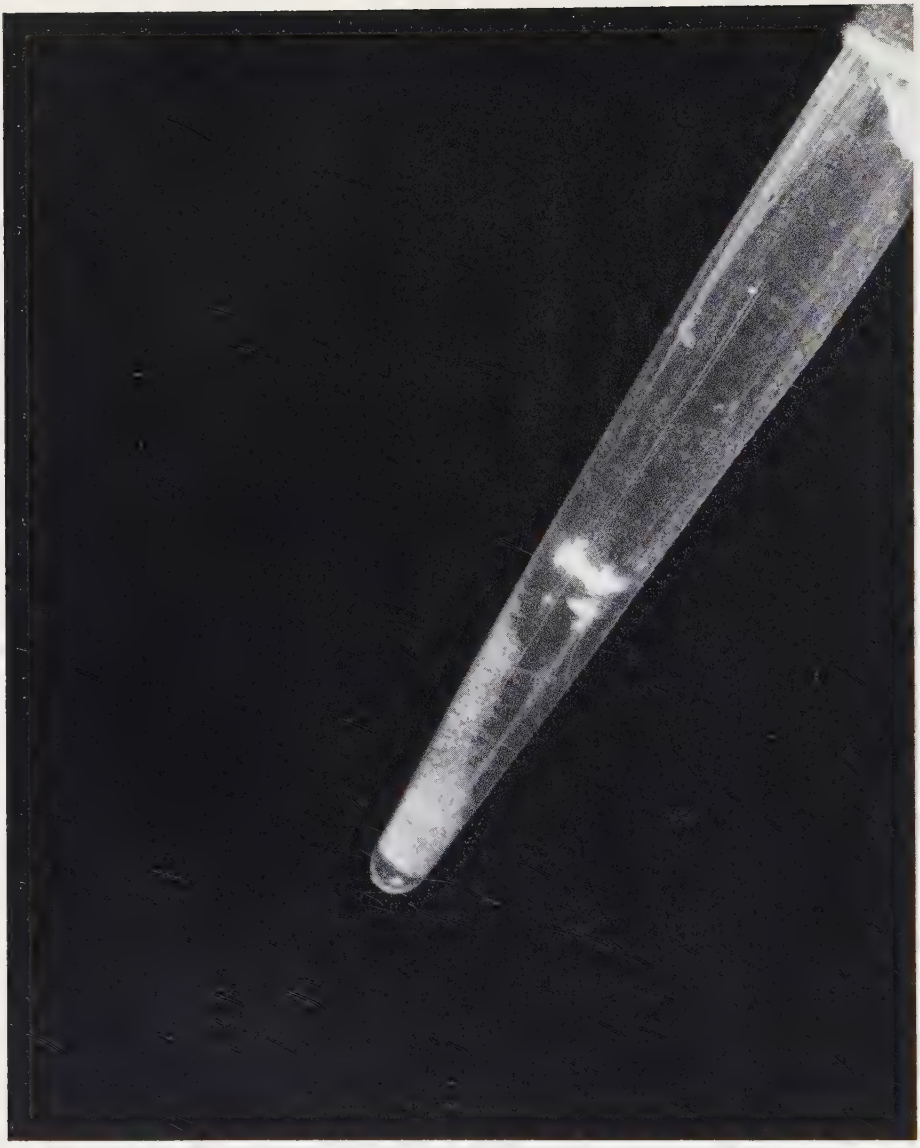


Fig. 1.11 Photograph of first curium compound (hydroxide) in bottom of microcentrifuge cone. Isolated in the fall of 1947. Magnified about 3-fold.

1.15 Continuing Contributions

Technologic and scientific interest in plutonium did not cease with the end of the war, of course. Operation of the Hanford Plant was taken over by the General Electric Company when the duPont Company withdrew at its own request. However, the duPont Company re-entered the business a few years later (in 1950) when it became the builder and later the operator of the huge Savannah River Plant, with its heavy-water moderated reactors, for the manufacture of plutonium. Plants for the manufacture of plutonium in quantity shortly began operation in England and in the USSR, and smaller production rates were soon achieved in France, to be followed by other countries. Research on the chemistry, metallurgy, nuclear properties, etc. of the element has continued at an accelerated pace. On the whole, this later work is distinguished from that done in wartime because of many important contributions from laboratories other than those in the United States, and because of an enhanced interest in those aspects of the chemistry and metallurgy of plutonium pertinent to the operation of reactors designed for the production of useful power, as opposed to the manufacture of fissile materials for nuclear weapons.

With the gradual relaxation of restrictions on declassification, many publications appeared (and are still appearing) based wholly or in part upon wartime research. In some cases these publications serve primarily to document more fully the early exciting chapters in the history of plutonium; often, however, they represent novel and important additions to the open literature.

It is quite impossible here to discuss fully the entire, or even the major part, of the postwar work on plutonium. It is intended, instead, only to indicate in a general way the sources and principal currents in this flow of effort.

1.15a Metallurgical Properties

Studies on the physical properties and metallurgy of elemental plutonium, initiated in the war years at the Metallurgical Laboratory in Chicago and pursued extensively at the Los Alamos site (as mentioned above), extended into the postwar years. Open pub-

lication of the results of this work was prohibited until 1954. At that time the results of the early American work on the allotropy of pure plutonium, carried out at Los Alamos under the direction of C. S. Smith and E. R. Jette, were published.

About the same time, the results of English work in this field, carried out at the Atomic Energy Research Establishment (AERE) at Harwell, Berkshire, England, by W. B. H. Lord, J. G. Ball, P. Mardon, J. A. Lee, and E. T. Adams, were published in the open literature. Additional material was declassified for the Geneva Conference on the Peaceful Uses of Atomic Energy, held in August 1955. Presented at this time were the extensive studies by A. S. Coffinberry and F. H. Ellinger of the Los Alamos Laboratory on intermetallic compounds of plutonium, and the wartime measurements of the vapor pressure of liquid plutonium done by O. C. Simpson and his associates of the Metallurgical Laboratory in Chicago.

Work by S. T. Konobeevsky of the USSR on the allotropic modifications of plutonium and on binary systems of the element with beryllium, lead, vanadium, manganese, iron, chromium, nickel, and osmium was presented at the conference of the Academy of Science of the USSR, in Moscow, July 1955, and was again presented, in part, at Geneva. Since then, important crystallographic studies of intermetallic compounds of plutonium have been published by O. J. C. Runnalls of the Chalk River Laboratory, Atomic Energy Canada, Ltd. Important metallurgical studies on plutonium have also been carried on by F. G. Foote and co-workers at the Argonne National Laboratory, H. M. Finniston and co-workers in Great Britain, and E. Grison and co-workers in France. A quite remarkable achievement by W. H. Zachariasen of the Department of Physics, University of Chicago, has been the elucidation of the complicated alpha-plutonium structure from X-ray diffraction powder data alone.

The metallurgical properties of plutonium are discussed further in Chapter 2, below (see Table 2.2).

1.15b Chemical Properties

Studies of the preparation and properties of compounds of plutonium have been carried out at all major centers of nuclear re-

search, often in connection with potential application to chemical processing of reactor materials. Such studies include early work by B. G. Harvey, H. G. Heal, A. G. Maddock, and E. L. Rowley of the Chalk River Laboratory on plutonium oxides, iodates, and sulfates; more recent investigations of the preparation and properties of some plutonium fluorides by J. K. Dawson, R. M. Elliott, R. Hurst, and A. E. Truswell of the AERE, Harwell, England; a study of crystalline plutonium nitrate by J. L. Drummond and G. A. Welch, also of Harwell; and a number of investigations on the chemically interesting compound, plutonium hexafluoride (PuF_6).

Plutonium hexafluoride had first been prepared by A. E. Florin at the wartime Metallurgical Laboratory in Chicago, but all work on this compound remained classified until the time of the Geneva Conference in 1955. At the Conference, B. Weinstock and J. G. Malm of the Argonne National Laboratory in Chicago and C. J. Mandleberg, H. K. Rae, R. Hurst, G. Long, D. Davies, and K. E. Francis of the British AERE presented summaries of the studies of this substance that had been carried out in the United States and England, respectively. The report by Weinstock and Malm covered work done by them and a number of their associates at the Argonne National Laboratory, including D. M. Gruen (magnetic susceptibility measurements), H. H. Claassen (Raman and infrared spectra), J. K. Brody, F. S. Tomkins, and M. S. Fred (absorption spectra), as well as the work of A. E. Florin, I. R. Tannenbaum, and J. F. Lemons at the Los Alamos Scientific Laboratory, and of N. J. Hawkins, H. C. Mattraw, and W. W. Sabol of the Knolls Atomic Power Laboratory (KAPL) of the General Electric Company at Schenectady, New York.

Plutonium hexafluoride is difficult to prepare and actually is unstable at room temperature with respect to decomposition into the tetrafluoride and fluorine. Fortunately, under proper conditions of storage the decomposition rate is slow. Nevertheless, it is a tribute to the skill of the workers mentioned that the compound has now been rather well characterized.

Compounds of plutonium with the nonmetallic elements of the first and second rows of the periodic table have potential utility in power technology because of their high density and refractory

character. Compounds of this class have been studied by A. S. Coffinberry and F. H. Ellinger of the Los Alamos Scientific Laboratory, by O. J. C. Runnalls of the Canadian Chalk River Laboratory, and by F. Brown, H. M. Ockenden, and G. A. Welch of the British AERE, Harwell.

The useful and chemically interesting plutonium hydrides, originally made at the wartime Metallurgical Laboratory, Chicago, to demonstrate the metallic properties of the first preparations of elementary plutonium—and also studied during the war by I. B. Johns, Jr., and co-workers of the Los Alamos Laboratory—have since been carefully reinvestigated by R. N. R. Mulford of the latter laboratory, and by Ockenden and Welch of Harwell.

W. H. Zachariasen continued, after the war, to make his excellent X-ray diffraction crystallographic identification of various plutonium compounds. Also of interest and importance, especially in the area of identification of plutonium compounds, is the work of E. Staritzky of the Los Alamos Laboratory in optical crystallography such as the determination of crystal habit, refractive indices, birefringence, etc.

Basic to the understanding of the chemical properties of plutonium ions in aqueous solution is a knowledge of the way in which the nature of the various species changes as the hydrogen-ion concentration of the solution is varied. Work on this problem may be traced back to microgram-scale work by K. A. Kraus at the Metallurgical Laboratory. These studies were continued by Kraus, J. R. Dam, and their co-workers at the Oak Ridge National Laboratory, and expanded to include a number of other actinide and nonactinide ions. As a result, quite unexpected equilibria between various polymeric species have been revealed. Somewhat parallel investigations by L. G. Sillén in Sweden have demonstrated the existence of other hydrolytic polymers of puzzling composition. The question as to why certain of these species have special stabilities is one of the most fascinating problems of present-day inorganic chemistry.

The hydrolytic behavior of plutonium may be regarded as a special aspect of the broader problem of the formation of complex ions of plutonium, a field in which J. C. Hindman and his group at the Argonne National Laboratory have made important contributions, as have M. Ward and G. A. Welch of the AERE,

R. E. Connick and his students at the University of California, and S. W. Rabideau and others at Los Alamos. Studies of complex-ion formation have generally been made by spectrophotometric or potentiometric methods. The precise evaluation of the potentials of the plutonium couples and the elucidation of the absorption spectra of ionic species are themselves fields of special interest.

Rabideau has carefully remeasured potentials of the plutonium couples, following earlier work by Connick and Hindman. The oxidation-reduction behavior of plutonium is conditioned by kinetic factors, which have been studied by Connick and co-workers, as well as by B. G. Harvey while he was at Chalk River.

The absorption spectra of plutonium ions, accurately determined by Connick and Hindman and by D. C. Stewart of the Argonne National Laboratory, are of analytical value as well as of theoretical interest in respect to the identification of the spectroscopic terms associated with the various transitions. Theoretical interpretations of certain transitions have been proposed by Gruen and Hindman, and more especially by C. K. Jørgensen in Copenhagen.

Large numbers of lines in the emission spectra of neutral and ionized gaseous plutonium have been recorded by workers at Berkeley, Argonne, Oak Ridge, and Harwell, but nothing approaching a complete term analysis has been achieved.

The chemical properties of plutonium are further discussed in Chapter 2, below.

1.15c Electronic Configuration

J. C. Hubbs, R. Marrus, W. A. Nierenberg, and J. L. Worcester at Berkeley in 1957 successfully measured the radiofrequency absorption spectrum of a beam of neutral plutonium atoms in a magnetic field. Their results are consistent with a $5f^6 7s^2$ configuration for the nonexcited neutral plutonium atom (see below, Table 2.10). The atomic beam resonance technique, adaptable to the use of trace quantities of radioactive species, bids fair to throw much light on the electronic configurations of all of the transuranium elements through fermium.

Very shortly after the end of the war, information concerning the electronic configurations of the ions of plutonium and other

actinide elements was sought by conventional magnetic susceptibility measurements. The earliest measurements on solutions were made by J. J. Howland, Jr., of the University of California Radiation Laboratory, in collaboration with M. Calvin. Careful measurements on solid compounds of plutonium, over an extended range of temperatures, were made by J. K. Dawson and G. R. Hall of the AERE, Harwell. Although there still remain some unsolved problems with respect to the detailed theoretical interpretation of gross magnetic susceptibilities of compounds of plutonium, on the whole, existing magnetic data suggest the presence of $5f$ electrons and strongly support the actinide concept of the transuranium elements.

The electronic structure of the PuO_2^{++} ion is of especial interest. The interpretation of the gross susceptibility of sodium plutonyl acetate, in terms of the electronic configuration of this PuO_2^{++} ion, remained obscure until the question of the Stark levels of the plutonium (VI) ion in the strong axial field existing in PuO_2^{++} was examined theoretically by the English physicists R. J. Elliott, J. C. Eisenstein, and M. H. L. Pryce. It then became apparent that the gross susceptibility of the powdered material might well be close to the measured "spin only" value, although the electronic configuration was $5f^2$. The question seems to have been resolved completely by the paramagnetic resonance measurements on a single crystal of the salt $RbPuO_2(NO_3)_3$ (diluted with $RbUO_2(NO_3)_3$) made by B. Bleaney of Oxford University in collaboration with P. M. Llewellyn, M. H. L. Pryce, and G. R. Hall, who showed that the magnetic anisotropy of the salt was that expected for a pair of f electrons in PuO_2^{++} occupying the magnetic substates ± 3, ± 2, with spins parallel.

1.15d The Related Elements Neptunium, Americium, and Curium

Some attention was devoted earlier in this chapter to the chemistry of neptunium, americium, and curium—elements closely associated with the early history of plutonium. The further developments in the chemistry of these elements, which have often shed additional light on our understanding of plutonium chemistry, will therefore be reviewed briefly. The first few milligrams of Np^{237} from the reactor source were isolated near the end of 1944 as the result

of special runs, designed for the extraction of neptunium, in the chemical extraction plant at the Clinton Laboratories. This recovered material which was normally lost in the waste in the unmodified Bismuth Phosphate Process was concentrated and isolated by a group headed by J. J. Katz, consisting of L. B. Magnusson, T. J. LaChapelle, J. R. Gilbreath, and W. C. Beard, Jr., who came from the Metallurgical Laboratory for this purpose. Gram amounts of Np^{237} were recovered at Hanford during several years following the war in a number of special runs in which the Bismuth Phosphate Process was modified so that the Np^{237}, which again normally appeared in the waste solutions and hence was lost, was recovered by using a process worked out at the Metallurgical Laboratory in a group under the direction of F. W. Albaugh and R. C. Thompson. The first of these so-called "IP Runs," named after I. Perlman who played a leading role in making the arrangements, occurred in May 1945, and these were followed by several others during the next few years. Since the solvent extraction procedures for the recovery of plutonium, in later use at Hanford and the Savannah River Plant, also do not normally recover the Np^{237}, special efforts were again necessary in order to make continuing recoveries of Np^{237}. The Am^{241} used for the study of americium has generally been recovered from Pu^{241}-containing plutonium in the various laboratories concerned, although later there has been some recovery in connection with the processing facilities involved in the production of plutonium. The Cm^{242} used for the study of curium has been produced by the neutron irradiation of Am^{241}, and its isolation has been the task of the individual laboratories involved. Later the more applicable isotopes Am^{243} and Cm^{244} (and heavier curium isotopes) have been employed; these are generally produced by intense neutron irradiation of Pu^{239} (or Am^{241}) in high flux reactors, followed by individual hot-laboratory isolation procedures.

In the United States, research on the chemistry of neptunium has been centered largely at the Argonne National Laboratory, where Hindman, D. Cohen, and various co-workers have carried out extended studies of absorption spectra, oxidation-reduction equilibria, reaction kinetics, and complex-ion formation of its aqueous ions. Here, also, low-temperature heat capacity measurements

on neptunium dioxide were carried out by E. F. Westrum, Jr., J. B. Hatcher, and D. W. Osborne.

Other work on neptunium, centered at Argonne, includes magnetic susceptibility measurements of solid compounds by Gruen and C. A. Hutchison, Jr., the solving of the structures of alpha- and beta-neptunium metal, by W. H. Zachariasen (of the University of Chicago), studies of neptunium hexafluoride by B. Weinstock and J. G. Malm, and the preparation of a higher neptunium oxide by J. J. Katz, Gruen, and their co-workers.

Notable contributions to neptunium chemistry from other U.S. laboratories are those by K. A. Kraus, of Oak Ridge, on the hydrolysis of neptunium ions, and the extended studies of chemical and optical properties of neptunium (V) carbonates by J. P. Nigon, R. A. Penneman, E. Staritzky, T. K. Keenan, and L. B. Asprey at Los Alamos. A very useful method for separating neptunium from plutonium by volatilization of $NpCl_4$ has been described by I. K. Shvetsov and A. M. Vorobyev of the USSR, while an ion-exchange method of separating neptunium from uranium and fission products was developed by the Swedish chemist, G. Johansson.

The determination of the paramagnetic resonance spectrum of NpO_2^{++}, in dilution in the crystal $RbUO_2(NO_3)_3$, by B. Bleaney of Oxford University was of great interest, as it served to clarify the question of the electronic configuration of this ion (showing it to contain a $5f$ electron).

Postwar work on the chemistry of americium and curium in the United States has been done mainly at the Los Alamos Scientific Laboratory and at the Department of Chemistry and the Radiation Laboratory of the University of California.

As mentioned earlier, it is much more difficult to prepare the higher oxidation states of americium than the corresponding states of plutonium. However, L. B. Werner and I. Perlman succeeded in oxidizing americium to the V state at Berkeley in 1948. The VI state was discovered by L. B. Asprey, S. E. Stephanou, and R. A. Penneman at Los Alamos in 1950. As yet, no solution of americium has been shown to contain an appreciable concentration of the IV state, which evidently is very rapidly reduced by water. Americium metal was first prepared at Berkeley by E. F. Westrum, Jr., and L. Eyring, who measured its bulk density.

Various aspects of americium chemistry have been examined by B. B. Cunningham, J. C. Wallmann and their co-workers and students at Berkeley. This work includes the determination of the crystal structure of alpha-americium metal and the detection of other allotropic modifications (in collaboration with P. Graf and D. H. Templeton), measurement of the standard heats of formation of the americium aqueous ions (in collaboration with L. Eyring, H. R. Lohr, and S. R. Gunn), magnetic susceptibility measurements on AmF_3 (with W. W. T. Crane), determination of the fluorescence spectrum of $AmCl_3$ in $LaCl_3$ (jointly with Gruen and J. C. Conway) and of $NpCl_3$ and $CmCl_3$ in $LaCl_3$ (with Conway and R. D. McLaughlin), determination of the absorption spectrum of hydrated $AmCl_3$ (with Conway and B. J. Stover), and an investigation of the vapor phase hydrolysis of $AmCl_3$ (with C. W. Koch).

A number of solid compounds of americium, including trihalides, were prepared by S. Fried on the microgram scale at the Argonne National Laboratory. The compound AmF_4, was first prepared at Los Alamos by L. B. Asprey and co-workers. R. A. Penneman, Asprey, and others at Los Alamos investigated the mechanism of oxidation of americium (III) to americium (VI) by peroxydisulfate, and also studied the disproportionation of americium (V). At the AERE, Harwell, G. R. Hall and others determined the stoichiometry of the americium sulfate-americium oxide conversion, while M. Ward and G. A. Welch investigated the oxidation of americium (III) to americium (VI) by iodic acid.

An investigation of the americium emission spectrum by M. S. Fred and F. S. Tomkins of the Argonne National Laboratory has enabled them to establish the ground state as having the electronic structure $5f^{7}7s^{2}$.

The study of the chemistry of curium was hampered for a long time owing to the very short half life of the isotope Cm^{242} (162 days), which for a number of years was the only isotope available in weighable amounts. Compounds of this isotope of the element were subjected to rapid destruction of crystal lattices, while aqueous solutions quickly built up relatively high concentrations of hydrogen peroxide. In spite of these difficulties, Wallmann, Cunningham, and Crane, at Berkeley, prepared metallic curium in 1952, and

D. C. Feay and Cunningham measured the stability constants of several fluoride complexes of Cm^{+3}, while Ward and Welch determined the association constant of the ion $CmCl^{+2}$.

A fairly extensive list of lines of the emission spectrum of curium (I) has been tabulated by Conway at Berkeley and Fred and Tomkins at the Argonne National Laboratory. Early observations of the absorption spectrum of aqueous Cm^{+3}, made by Werner, I. Perlman, and Conway, were shown to be in error at shorter wave lengths, because of absorption by hydrogen peroxide.

Progress in curium chemistry is becoming more rapid, owing to increasing availability of the isotope Cm^{244} (19-year half life). Using this isotope, Asprey, F. H. Ellinger, S. Fried, and W. H. Zachariasen succeeded in preparing and identifying a higher oxide (CmO_2). Asprey has also succeeded in preparing and identifying a higher fluoride (CmF_4) of this element. P. R. Fields, B. Smaller, A. M. Friedman, and W. Low, at the Argonne National Laboratory, and C. D. Jeffries, J. C. Wallmann, Cunningham, M. Abraham and R. W. Kedzie, at Berkeley, have been able to observe the paramagnetic resonance spectrum of $CmCl_3$ in $LaCl_3$, and find that the spectrum is consistent with the expected electronic ground-state configuration of $^8S_{7/2}$ for Cm^{+3}.

As is clear from the preceding remarks, much remains to be done in research on the chemistry of both americium and curium. The chemical properties of neptunium, americium, and curium are further discussed in Chapter 2, below.

1.15e The Development of Chemical Processing Methods

An increasing share of attention in the major centers of nuclear research was devoted in the postwar years to problems of chemical processing of irradiated reactor fuel elements.

Successful as the Bismuth Phosphate Process had been in providing the United States with plutonium for nuclear weapons, it offered no efficient means of recovery of the highly valuable uranium left after plutonium extraction. As world competition in the nuclear-power field developed, reactor economics became of paramount importance. All countries hoping to utilize nuclear fuels for industrial power sought to devise cheap and efficient means for the

separation, decontamination, and recovery of useful components from irradiated fuel.

Although it had early been recognized that processes based on other than precipitation methods probably would lead ultimately to higher efficiency and cheaper costs, major efforts to realize such processes were delayed until near the end of and after the war. The success of these various efforts was revealed for the first time at the Geneva Conference on the Peaceful Uses of Atomic Energy in August 1955.

The nonprecipitation processes described there may be roughly divided into four classes: (1) solvent extraction, (2) ion exchange, (3) pyrometallurgy and pyrochemistry, and (4) fractional distillation. More often than not, a complete processing scheme may be most economically constructed by using combinations of these various processes.

Solvent extraction. In solvent extraction processing, the desired chemical separations are brought about by a series of liquid-liquid phase contacts under conditions which favor selective partitioning of a particular element (or elements) in one phase, as compared with another. (In precipitation processing, similar separations can be achieved by favorable partitioning between a liquid phase and a precipitated solid phase.) Solvent-extraction processing of irradiated nuclear fuels is very attractive from an engineering standpoint, as efficient separations, high recoveries, and low maintenance costs are readily achieved once the basic problem of finding suitable solvents has been conquered.

From about 1945 onward, the search for such solvents and extraction agents was pursued vigorously in the United States, England, Canada, France, and, presumably, the USSR, although no Russian work in this field has been published at the time of this writing. Of many organic substances which may be used to separate the components of irradiated fuel elements in dilute solution and at low levels of activity, very few appear to meet the criteria of efficiency, high chemical stability, and ready recoverability demanded for economical processing of concentrated reactor fuel solutions. The substances which appear most useful for this purpose are tributylphosphate (TBP), methyl isobutyl ketone (hexone), and the-

noyltrifluoroacetone (TTA). The Redox and TTA processes, which are based on the use of the latter two reagents respectively, had their start in wartime research and were described above. Such material can be used for processing only after fuel elements withdrawn from the reactors have been allowed to undergo a long period of radioactive "cooling" to permit the decay of short-lived radioactivities.

The use of tributylphosphate in solvent-extraction separations similar to those connected with the maintenance of reactors was described by J. C. Warf of the Ames Laboratory at Iowa State College in an Atomic Energy Commission declassified document released in 1949, but describing work done in 1947. A subsequent publication in 1950 by M. R. Anderson, also of Iowa State College, outlined a method of extracting thorium nitrate from an aqueous solution, using a mixture of butyl phosphate and butyl ether. In the following year R. L. Moore discussed the mechanism of extraction of uranium by TBP. Thus the potential usefulness of TBP for processing seems to have been indicated in the United States at least as early as 1947, and probably was universally appreciated by 1951.

The exploitation and development of the use of the reagent in practical processing methods required a great deal of further effort, however. In the United States, the Oak Ridge National Laboratory played a major role in this development, although important contributions were made by many individuals at other sites. Responsibility for the work at Oak Ridge was largely in the hands of J. R. Flanary, F. L. Culler, Jr., F. R. Bruce, and A. T. Gresky, with C. V. Ellison, T. C. Runion, and W. B. Lanham initially responsible for the form in which this process was developed for large-scale use.

In one important modification of a TBP extraction scheme, known as the "Purex Process," irradiated uranium fuel elements are dissolved in nitric acid and the solution extracted with a hydrocarbon diluent containing about 20% TBP. Both uranium and plutonium pass almost quantitatively into the organic phase, leaving most of the fission-product activity in the water solution. The organic phase is then contacted with a second aqueous phase containing a reducing agent to reduce plutonium to the III state,

which then transfers quantitatively to the aqueous phase. Finally, uranium is recovered by contacting the TBP-hydrocarbon phase with a third aqueous phase containing only a very slight amount of nitric acid. In practice, good recoveries of uranium and plutonium and very high decontamination from fission products are achieved by various recycling and scrubbing operations. The Purex Process found a major use at the Savannah River Plant.

By a second method—the "Thorex Process," developed largely by A. T. Gresky and co-workers—TBP extractions are used to separate uranium, thorium, protactinium, and fission products. This separation may be applied to the recovery of valuable materials produced in the operation of "breeder" reactors operating on the thorium-U^{233} cycle. A third TBP process separates uranium and fission products, as required for the processing of enriched uranium fuels, while a fourth is applied to the recovery of uranium from the "waste" uranium-fission product mixtures accumulated during the wartime and later operation of the Hanford Bismuth Phosphate Process.

A great deal of work on TBP extractions has been done outside of the United States, as, for example, the basic studies of chemical species involved in such extractions done at the AERE, Harwell, England, by H. A. C. McKay, E. Glueckauf, and their collaborators, K. Alcock, D. Scargill, F. S. Martin, and H. R. C. Pratt. In France, TBP has been used in processing reactor fuels by a method developed under the direction of B. Goldschmidt, P. Regnaut, and I. Prevot of the Commissariat à l'Energie Atomique.

Although organophosphate extractants at the time of the present writing seem to be the most highly favored reagents for reactor processing, the methyl isobutyl ketone (hexone) used earlier still figures prominently in many schemes. Hexone processes are basically quite similar to the various TBP methods outlined previously, the chief differences being that plutonium must be oxidized to the VI state before the initial extraction, and a salting agent (aluminum nitrate) is required to ensure quantitative extraction of plutonium and uranium into the hexone phase.

The Redox Process, described above, is a method which uses hexone on fuel elements made from natural uranium. The use of hexone for the recovery and purification of plutonium from various

mixtures was initiated in 1944 and 1945 at the Metallurgical Laboratory in Chicago by L. R. Dawson. Hexone processes applicable to chemical separations needed in reactor operation were developed by W. J. Blaedel, H. H. Hyman, S. Lawroski, and I. J. Schaffner at the Argonne National Laboratory; E. L. Zebroski, J. F. Thomas, and G. Feher, of the Knolls Atomic Power Laboratory, Schenectady, New York; and F. L. Culler, Jr., and others at Oak Ridge. The Redox Process found its outstanding use at Hanford.

As in the case of TBP, hexone processing has been investigated independently in foreign laboratories, notably by J. M. Fletcher, H. A. C. McKay, and others at the AERE, Harwell, and by B. Goldschmidt, P. Regnaut, and I. Prevot of the French atomic energy installation at Saclay, near Paris.

In the systems discussed above, extraction into the organic phase is associated with the formation of neutral molecular species which solvate with the extractant. Neutral complexes of uranium, plutonium, etc. may also be formed by the addition of various organic complexing agents, and these complexes often have very high solubilities in organic liquids. An example of such a complex-forming reagent described in an earlier section is TTA, which combines with Pu^{+4} with great affinity and at the proper acidity promotes extraction of the plutonium into water-immiscible organic liquids such as benzene.

TTA was developed as a general chelating agent by M. Calvin of the University of California toward the end of and just after the war and has been rather thoroughly studied by process chemists and chemical engineers—in the United States chiefly by Culler, J. R. Flanary, and F. R. Bruce of Oak Ridge. A somewhat serious problem in large-scale processing with TTA is the slow rate of complex formation, which impairs the efficiency of countercurrent extraction.

Complexing agents other than TTA which have been examined for potential use in nuclear technology include cupferron (ammonium nitrosophenylhydroxylamine), neo-cupferron (ammonium alpha-naphthyl-nitrosohydroxylamine), and tetrabutylamine nitrate—all of which were studied by E. Haeffner, G. Nilsson, and A. Hultgren at the Aktieboleget Atomenergi, Department of Physics, Stockholm, Sweden—and acetylacetone, examined by J. Ryd-

berg of the Research Institute of National Defense, Stockholm, Sweden.

Ion exchange. As indicated earlier, ion exchange techniques were studied from the very beginning as a possible method for separating plutonium from the uranium and fission products. Also, as will be shown in the next chapter, these techniques offer a method for separating even such closely similar elements as are found in the lanthanide and actinide series. It might well be expected that ion exchange would find useful applications in the chemical processing of nuclear fuels, and such is the case. It was not until near the end of the war that synthetic organic exchange materials of good selectivity, large capacity, and high chemical stability became available on a commercial basis.

As this development was occurring, the Clinton Laboratories took an early interest in applying ion exchange to the separation of fission-product materials, especially the rare earths. Important contributions were made by G. E. Boyd, J. Schubert, A. W. Adamson, W. E. Cohn, E. R. Tompkins, P. C. Tompkins, J. X. Khym, C. D. Coryell, J. A. Marinsky, and L. E. Glendenin. (The work of the latter three investigators resulted in their discovery of promethium, the element with the atomic number 61.) Further development of ion-exchange methods for processing application was carried out by D. R. Ferguson, P. N. Hackenreich, and I. R. Higgins. Other individuals who have contributed notably to the development of useful ion exchange techniques include K. A. Kraus of Oak Ridge; our group at the University of California Radiation Laboratory; S. Lawroski at the Argonne National Laboratory; D. A. Orth at the Savannah River Laboratory, Aiken, South Carolina; and N. E. Ballou and co-workers at the U. S. Radiological Defense Laboratory. Important studies of ion exchange processing methods applicable to reactor materials have been reported by A. Chesné and P. Regnaut of the French Commissariat à l'Energie Atomique.

Pyrochemical and pyrometallurgical methods. One rather important drawback to all of the processes thus far considered is that they can be applied only to relatively "cool" nuclear fuels—that is, reactor elements which have been in storage for a period of around 100 days after removal from the reactor. Continuous reactor operation

under these circumstances demands the maintenance of a relatively high inventory of fissionable materials, since at any one time a substantial part of the materials will be in storage. A second objection to conventional chemical processing is that fuel materials are recovered as salts, which must often be reconverted to the metal before return to the reactor.

These difficulties may be overcome to a substantial degree by pyrometallurgical and pyrochemical processing, the distinguishing feature of which is the processing of the fuel elements as liquid metals at high temperatures. After decontamination, the liquid metals need only to be recast in solid form, reclad, and returned to the pile or used in other form. In these processes, chemical and radiochemical purification to the degree achieved by conventional chemical processing methods is not intended, since the chief purpose in pyrometallurgical and pyrochemical processing is to remove the bulk of fission-product poisons and thus to allow a quick return of the fuel to the reactor.

Pyrometallurgical or pyrochemical processing, as applied to uranium fuels, makes use of one or more of the following steps: (1) separation of some fission products at high temperature by volatilization, (2) extraction of other fission products by contacting the liquid uranium with fused salts, (3) extraction of still other fission products by contact of the molten uranium with immiscible liquid metals, such as silver or magnesium, and (4) further decontamination by controlled slagging, that is, by the controlled addition of oxygen or carbon to the liquid metal for the purpose of forming oxides or carbides of undesirable contaminants that are more stable than the uranium carbides or oxides.

In the development of pyrometallurgical processing, an early paper on the high-temperature thermodynamics of uranium, plutonium, and the fission-product elements by L. Brewer of the Department of Chemistry, University of California, played a very important part.

Practical experiments in process applications of pyrometallurgy have been carried out in various United States laboratories. Valuable studies of fission-product removal by volatilization and oxidative slagging have been made by H. M. Feder, H. C. Chellew, M. Ader, C. Cushing, and co-workers at the Argonne National

Laboratory, while at the Ames Laboratory, Iowa State College, A. F. Voigt, F. H. Spedding, I. B. Johns, Jr., P. Chiotti, A. H. Daane, and co-workers have studied the extraction of fission products and plutonium from molten uranium, using molten magnesium and molten silver as extractants.

A general investigation of pyrometallurgical and pyrochemical processing methods has been reported by E. E. Motta, D. D. Cubicciotti, Jr., and co-workers at the North American Aviation Corporation at Los Angeles, California. These investigators have concentrated on the use of UF_4 for fused salt extractions, and magnesium as the liquid-metal extractant.

At the Brookhaven National Laboratory, interest in pyrometallurgical and pyrochemical methods has centered around their possible application to processing problems associated with the operation of a liquid-metal reactor, containing a solution of uranium, magnesium, and zirconium in liquid bismuth as the core, with a surrounding blanket containing a slurry of $ThBi_3$ in liquid bismuth; F. T. Miles and co-workers have contributed to this development. O. E. Dwyer, R. J. Teital, and R. H. Wiswall, Jr., of Brookhaven National Laboratory propose a continuous processing of the reactor by volatilization of some fission products from molten bismuth, extracting others with fused UCl_3 and resorting infrequently to conventional chemical processing, as necessary.

Plutonium extraction from molten uranium by molten silver and by fused uranium tetrafluoride is involved in a process which has been under investigation at the Chalk River Laboratory in Canada by A. M. Aiken, D. E. McKenzie, and co-workers. Various slagging and chlorination procedures have been investigated by F. S. Martin, G. L. Miles, and co-workers at the AERE, Harwell, England.

It appears at this time that pyrometallurgical and pyrochemical processing methods will find increasing application in the technology of future power reactor operation.

Fluoride distillation methods. It need scarcely be said that no form of chemical processing now known will restore reactor fuels which have become seriously depleted in their fissionable isotope content. Recognizing that in many cases it will be necessary to enrich such depleted fuels by isotopic separation, J. J. Katz, H. H. Hyman, and

R. C. Vogel of the Argonne National Laboratory have advocated the use of a fluoride distillation method for the chemical processing of uranium fuels, since the decontaminated element would then emerge from the process in the form of volatile UF_6, directly suitable for re-enrichment by a diffusion process.

Interest in fluoride volatility processes extends back as far as the wartime work of H. S. Brown and co-workers, carried out at the Chicago Metallurgical Laboratory, as mentioned above. Brown studied the processing of irradiated uranium by treatment with elemental fluorine and observed good separations of uranium from plutonium and many fission products. Because of the very formidable technical difficulties of using elemental fluorine, the volatility process did not then receive very favorable attention.

One of these technical difficulties, that of dissipating the heat of fluorination using a gaseous reagent, was largely solved by the work of H. J. Emeleus of Cambridge University, England, on the properties of the interhalogen compounds of fluorine. Among these substances, bromine trifluoride and bromine pentafluoride proved to be admirably suited for the rapid, yet safe and controlled, liquid phase fluorination of uranium fuels. Elemental fluorine is still required for the production of the halogen fluoride, but the elimination of noncondensible fluorine from the fuel processing system results in simpler and more economical design.

Much work has been done at the Argonne National Laboratory by Katz, Hyman, Vogel, and co-workers on the fluoride distillation method employing fluorinating agents such as bromine trifluoride. A method which employs chlorine trifluoride has been investigated by R. A. Gustison and co-workers at Oak Ridge. Other programs of this type have been initiated by E. Lofthouse and co-workers in England, W. R. Page and co-workers at Brookhaven National Laboratory, and E. E. Motta and co-workers at the North American Aviation Company in Los Angeles. Later investigations on a somewhat larger scale have involved many additional chemists and engineers at several of these sites. R. Steunenberg and W. Meccham, working with Vogel, have been supervising a large program at the Argonne National Laboratory, while O. E. Dwyer, G. Strickland, and others at Brookhaven and R. Leuze and others at Oak Ridge have been involved in such continuing investigations.

Cost estimates indicate that a fluoride volatility process would compete economically with solvent-extraction or ion-exchange methods, and it may well be that future processing methods, especially of enriched uranium fuels, will make extensive use of the fluoride method.

In conclusion, this brief survey of chemical processing has intended to point out that chemists and chemical engineers are playing a vital part in the efforts of scientists to bring to the world the benefits of cheaper and more abundant power drawn from nuclear sources.

1.15f Nuclear properties

The wartime discoveries of the plutonium isotopes, Pu^{234}, Pu^{237}, Pu^{238}, Pu^{239}, Pu^{240}, and Pu^{241}, have been supplemented by the discoveries of a number of additional isotopes, so that all isotopes from Pu^{232} to Pu^{246}, inclusive, are known. The radioactive properties of all of these are listed in the Appendix, below (together with the radioactive properties of all of the known transuranium nuclides). Utilizing U^{233} and U^{235} as target materials, D. A. Orth and K. Street, Jr., of the University of California Radiation Laboratory, produced and identified, in 1951, two new short-lived isotopes of plutonium, Pu^{235} and Pu^{232}. The former was produced in the 60-inch cyclotron, while the latter was made with the new 184-inch cyclotron, a machine whose completion was a great stimulus to this program because its high-energy particles were able to excite many new nuclear reactions which previously had lain beyond the "energy barrier." Another neutron-deficient isotope, Pu^{233}, was identified by T. D. Thomas, R. Vandenbosch, R. A. Glass, and the author in 1956 as the result of a helium-ion reaction upon U^{233}, using the 60-inch cyclotron. That little detailed information on the nuclear properties of these isotopes is as yet available is due mainly to the experimental difficulties imposed by their short lifetimes and low production yields.

Several "heavy" isotopes of plutonium have been produced both by cyclotron and pile technique. S. G. Thompson, Street, A. Ghiorso, and F. L. Reynolds reported, in 1950, the synthesis of long-lived Pu^{242} from pile neutron irradiation of Pu^{241}. Still heavier and, at this time, the longest-lived, isotope of plutonium is Pu^{244},

discovered in bomb debris in 1954 by M. H. Studier, P. R. Fields, P. H. Sellers, A. M. Friedman, C. M. Stevens, J. F. Mech, H. Diamond, J. Sedlet, and J. R. Huizenga, at the Argonne National Laboratory. The isotope Pu^{242}, usually produced as the result of intense slow neutron irradiation of Pu^{239}, is a good starting point for the production of transplutonium nuclides by slow neutron irradiation.

Three short-lived "heavy" isotopes of plutonium are known, all of which decay by negative beta-particle emission. The isotope Pu^{243} was produced in 1951 at the Argonne National Laboratory and at Berkeley (J. C. Sullivan, G. L. Pyle, Studier, Fields, and W. M. Manning at Argonne; and Thompson, Street, Ghiorso, and Reynolds at Berkeley) by neutron irradiation of Pu^{242}. The irradiation of Pu^{244} with pile neutrons has also produced Pu^{245}, reported in 1955 by C. I. Browne, D. C. Hoffman, W. W. T. Crane, J. P. Balagna, G. H. Higgins, J. W. Barnes, R. W. Hoff, H. L. Smith, J. P. Mize, and M. E. Bunker of the Los Alamos Scientific Laboratory and the University of California Radiation Laboratory at Livermore; and Fields, Studier, Friedman, Diamond, R. Sjoblom, and Sellers of the Argonne National Laboratory. The isotope Pu^{246} was discovered in the debris of the "Mike" thermonuclear explosion late in 1952 by D. W. Engelkemeir, Fields, S. Fried, G. L. Pyle, Stevens, L. B. Asprey, Browne, H. L. Smith, and R. W. Spence of the Argonne National Laboratory and the Los Alamos Scientific Laboratory.

The beta decay of 13-year Pu^{241} is interesting because of its extremely low energy; only 20 kilovolts of energy (about equal to the difference in total electron-binding energy between the parent Pu^{241} and the daughter Am^{241}) are released in the beta transition. Thus the Pu^{241} nucleus is the same weight as the Am^{241} nucleus within a couple of kilovolts, and the beta decay energy comes largely from the difference in total electronic binding energy.

Much study has been made of the decay properties of Pu^{239}, and a very interesting dilemma concerning these properties has been solved. Three of the alpha decay groups had been identified by F. Asaro and I. Perlman in Berkeley and by L. L. Gold'in, G. I. Novikova, and E. F. Tretyakov in the USSR as populating a particular set of energy levels (in the daughter nucleus U^{235}) which

constitute a single rotational band (see below, Chapter 3). The lowest member of this band, with nuclear spin I equal to $\frac{1}{2}$, as given by A. Bohr, P. O. Fröman, and B. R. Mottelson, was not, however, the ground state of U^{235}, since the ground-state spin had previously been determined to be $\frac{7}{2}$. Yet no gamma transition was observed to take place between these two very different levels (the levels with I equal to $\frac{1}{2}$ and $\frac{7}{2}$), and the Pu^{239} decay scheme remained mysteriously uncertain. The existence of a nuclear isomer of type $E3$ was predicted by I. Perlman on experimental and theoretical grounds, and in 1957 such an isomer was actually identified by Asaro and Perlman at Berkeley and by J. R. Huizenga, C. L. Rao, and D. W. Engelkemeir at Argonne. Observed as a result of the collection of recoil nuclei from Pu^{239} alpha decay, this isomer has a half life of 26.5 minutes and seems to have an energy of excitation under 100 electron volts, thus establishing the lowest energy reported to this date for a nuclear excited state. It was thought that these isomeric levels might be characteristic of 143 neutrons, and a successful search was made by F. S. Stephens, Jr., Asaro, S. Amiel, and Perlman for similar isomers in Pu^{237}. In this isotope the $\frac{1}{2}+$ isomer state was found to have a half life of 0.18 second and to decay to the $\frac{7}{2}-$ ground state by an $E3$ transition of 145-kev energy.

The energy levels of Pu^{239} itself have received intensive study, from the beta decay of Np^{239}, from the electron capture decay of Am^{239}, and from the alpha decay of Cm^{243}. The experiments at Berkeley of J. M. Hollander, W. G. Smith, and J. W. Mihelich on the decay of Np^{239}, and the experiments at Harwell by J. O. Newton on the Coulomb excitation of Pu^{239}, in which high-resolution beta spectrographs were used, show that the low-lying states in Pu^{239} constitute an "irregular" rotational band (with $K = \frac{1}{2}$) whose energy spacings do not follow a simple $I(I + 1)$ dependence. (These considerations and this nomenclature are explained in some detail in Chapter 3.) The properties of this band were found to correlate well with the Bohr-Mottelson nuclear model which describes theoretically some of the properties of nuclei in this region. From the alpha decay of Cm^{243}, Asaro, Thompson, Stephens, and Perlman have observed several new energy levels in Pu^{239}. At present, the energy level scheme of Pu^{239} seems to be fairly well understood, and

has provided an interesting testing ground for some of the features of the Bohr-Mottelson model.

The fast and slow neutron fission properties of Pu^{239} have received considerable attention, as is not unexpected in the case of an isotope so important in the field of fission energy. The important property, the thermal neutron fission cross section, has been investigated extensively, and a "world consistent" value, obtained by D. J. Hughes and R. B. Schwarz by considering data from a number of countries, is 738 barns. The spontaneous fission rates of the even-even isotopes Pu^{236}, Pu^{238}, Pu^{242}, and Pu^{244} have been measured, and several other characteristics of this process determined for a number of these isotopes.

It has long been known that the mass yield distribution curve from the slow neutron-induced fission of Pu^{239} has a double-humped shape, but, as the result of more careful work, a "fine structure" has been observed in the smooth curve both by radiochemical and mass spectrometric methods in the work of S. Katcoff and co-workers, L. E. Glendenin and E. P. Steinberg, H. G. Thode and co-workers, and others. These points of enhanced fission yield have been interpreted in terms of closed nuclear shell effects, such as: (1) modes of fission are preferred in which one of the primary fragments has a closed shell of neutrons or protons and (2) additional boil-off of neutrons occurs from fission products having a neutron or two in excess of a closed shell.

Of much interest is the energy distribution of fission fragments, and much effort is presently being directed toward gaining an understanding of the mechanism of energy release and distribution in fission. Measurements of the energies of Pu^{239} fission fragments from neutron irradiation have been made by R. B. Leachman and co-workers at the Los Alamos Laboratory and by D. C. Brunton and G. C. Hanna, and J. S. Fraser and J. C. D. Milton and co-workers at the Chalk River Laboratory, as well as by others. Particular fission modes have been identified, and correlations have been made of the variation in kinetic energy of a given mode with its neutron and gamma ray emission properties.

1.15g Energy Source

Plutonium in the form of the isotope Pu^{239} has great importance as a source of energy for use in both nuclear weapons and nuclear power reactors.

The attainment of the wartime goal of the Metallurgical Project, culminating in the successful test of the plutonium weapon at Alamogordo, New Mexico, on July 16, 1945, and its actual use at Nagasaki, Japan, on August 9, 1945, is a well-known part of the plutonium story. The energy released by such explosion of the plutonium in the weapon was equivalent to that released in the explosion of about 20,000 tons of TNT. It is beyond the scope of the present account to describe the continuing contributions that have been made to plutonium weapon technology. Many improvements have been made in the size, the range of energy release, the efficiency, and the versatility of the weapon as the result of further research and tests. At the end of the war, upon the departure of J. R. Oppenheimer, N. E. Bradbury became the Director of the Los Alamos Laboratory, which continued to be operated by the University of California and now has the name "The Los Alamos Scientific Laboratory." Another United States nuclear weapons laboratory was created in the summer of 1952; this is the Livermore Laboratory, with H. F. York as the Director, and is a part of the University of California Radiation Laboratory, under the direction of E. O. Lawrence. Substantial nuclear weapons laboratories are also to be found in the USSR and in England, with the former making its first successful test of such weapons in the fall of 1949, and the latter in 1952. All three countries have expanded their fission-weapon programs to include the research on, the building of, and the testing of thermonuclear weapons. The production of nuclear weapons is an objective in other countries as well, and it is within their capabilities.

The Pu^{239} can also be used as a source of energy in power reactors, because the tremendous amounts of energy, released instantaneously in the nuclear weapon, can be released in a slow, controlled fashion as well. Such reactors operating primarily with Pu^{239} in the fuel elements have not been built at the time of this writing. Reactors operating on U^{235} supplemented by Pu^{239} formed

simultaneously from U^{238} by the absorption of neutrons are of increasing importance, and it is in this capacity that Pu^{239} is going to play an important role. Such a reactor is said to be "regenerative" and makes possible the indirect use of nonfissionable but "fertile" U^{238} as nuclear fuel, hence broadens the potential of uranium as a fuel beyond that of the rare isotope U^{235}. A reactor operating on Pu^{239} and generating from U^{238}, at the same time, more Pu^{239} than it consumes is a "breeder" reactor. (A similar possibility exists with nonfissionable thorium (Th^{232}) and the fissionable U^{233} produced by the absorption of neutrons in the thorium.)

There are, however, a number of very difficult problems to solve, largely engineering problems, before we can have economically competitive nuclear power. Such machines must run at high temperatures in order that the energy may be extracted usefully and efficiently, and this means that there will be many problems involving materials of construction, corrosion, and so forth. The materials of construction must be chosen from those whose neutron absorption is small in order to meet the demands of neutron economy; this limits the choice to uncommon substances. Adequate coolants that do not absorb many neutrons must be found, and methods for control of the reaction must be assured. Adequate fuel elements must be developed for some systems, which involves the solution of difficult metallurgical problems, and extraordinary heat transfer problems must be solved. It will be necessary to develop very efficient procedures to purify plutonium and uranium (i.e. separate or "decontaminate" partially spent fuel from fission products) and also to repurify these materials in order that unburned fuel may be used again, a matter which is of especial importance to breeder reactors. The problem of completely safe disposal of tremendous quantities of radioactive waste products is also a very difficult one. These problems will be solved, however, and nuclear power will be developed and used because of its advantages and because of the impending depletion of the other sources of fuel.

Neutron economy is of prime importance to a regenerative or breeder reactor. Since one neutron from each fission is always used up to produce a new fission reaction in order to sustain the chain reaction and another is needed for the formation of another fissionable atom, it is possible to breed more fuel than is burned only when

the number of neutrons produced by each fission exceeds two by a fair margin, because some neutrons are wasted through escape or absorption in structural and other materials. The imposition of this condition makes it clear that breeding in the Pu^{239}-U^{238} system will probably be possible only in a reactor operating on the fission of Pu^{239} with fast neutrons. In the case of slow neutrons, too many are lost by absorption to form Pu^{240} (although some neutrons are regained in the fission of highly fissionable Pu^{241} formed by the absorption of another neutron in Pu^{240}, thus involving a more complicated system whose regenerative qualities are worthy of further study). The Argonne National Laboratory, involving the work of W. H. Zinn, H. V. Lichtenberger, and co-workers, has built experimental breeder reactors to test the neutron economy of such fast neutron power sources. The first such experimental breeder reactor, constructed at the National Reactor Testing Station in Idaho, demonstrated that it is possible to burn U^{235} in such a manner as to form more Pu^{239} (than the consumed U^{235}) from U^{238}. Later such experimental breeder reactors will operate on Pu^{239} and will test the feasibility of true power breeding, i.e. the production of more Pu^{239} (from U^{238}) than is burned during the production of usable power. A similar test of the Pu^{239}-U^{238} breeding cycle in connection with power production is part of the program in Great Britain's nuclear power station at Dounreay, Scotland; this approach is also under study at Harwell, where reactors named "Zephyr" and "Zeus" are used to study the nuclear properties of fast neutron breeder reactors. The first operation of a reactor, called "Clementine," using Pu^{239} as the fuel took place at the Los Alamos Laboratory.

Besides the investigation of solid plutonium metal and plutonium alloys as possible fuel elements in many laboratories in America, Europe, and the Soviet Union, a number of systems using molten plutonium or plutonium alloys, mixed oxides, and other chemical forms of plutonium as the fuel form are under investigation. Thus metallic plutonium and its intermetallic compounds and other possible forms are under intensive investigation.

The future will see the development of Pu^{239} as a source of industrial power, covering the gamut from its supplemental use *in situ* (due to production from U^{238}) during the burning of U^{235} in natural

uranium or U^{235}-enriched uranium, to its use in concentrated form in the fuel elements. The problems mentioned above will be solved for reactor systems of various types in conjunction with proper chemical procedures. An extremely important consideration in the use of Pu^{239} will be its unfortunate extraordinarily poisonous character, due to its high alpha radioactivity and physiological behavior upon ingestion. This will, in most instances, have a large effect on the choice and design of the particular system to be used. This factor, taken in conjunction with the fission-product waste-disposal problem, will place a premium on systems that avoid complete decontamination procedures, and perhaps avoid wet decontamination procedures; and that avoid, insofar as possible, complicated metallurgical procedures in the decontamination cycles. Regenerative systems that are short of being breeders and avoid chemical reprocessing may be attractive in many instances.

1.16 Publication

Accounts of the large amount of work done and results obtained on the Metallurgical Project were published in thousands of secret wartime reports. Most of these that have worthwhile scientific data in them, except those directly related to weapons, have been declassified. Their preliminary nature and the haste with which many were written makes them a poor ultimate source of information. Fortunately, a good portion of the essential data was published in a more coherent fashion in various ways after the war. One of these methods of publication was the Plutonium Project Record of the National Nuclear Energy Series published by the McGraw-Hill Book Company. R. S. Mulliken was in charge of the planning and implementation of this series, and he had the early help of L. L. Quill, E. Rabinowitch, and H. H. Goldsmith. J. C. Warner also made important contributions to the organization of this huge writing task. H. D. Young served as technical editor and then, in the summer of 1946, became general editor for the period that saw the completion of writing, declassification, and actual publication of the volumes. The over-all responsibility for the publication of this record, as well as that of other volumes covering work done in connection with the Manhattan District, was centered in the Atomic Energy Commission's Technical Information Division,

headed by A. F. Thompson. The volumes of especial interest from the present standpoint are Volume 14A, *The Actinide Elements*, edited by J. J. Katz and the author; Volume 14B, *The Transuranium Elements: Research Papers*, edited by Katz, W. M. Manning, and the author; Volume 5, *The Chemistry of Uranium*, edited by Katz and E. Rabinowitch; Volume 9, *Radiochemical Studies: The Fission Products*, edited by C. D. Coryell and N. Sugarman; Volume 17A, *Production and Separation of* U^{233}, edited by L. I. Katzin and the author; and Volume 17B, *Production and Separation of* U^{233}, *Collected Papers*, edited by Katzin. The latter two were published by the Office of Technical Services, Department of Commerce, Washington, D. C.

For a number of years following the war, some of the basic research work on plutonium was subject to rather long delay before it could be declassified. However, the situation has gradually reached the point where basic research results may now be published almost as soon as they are obtained, and this traditional publication procedure seems to apply to all parts of the world. The Conference on the Peaceful Uses of Atomic Energy held in Geneva, Switzerland, in 1955 led to the declassification and publication in its Proceedings of much information on the separation processes for plutonium and its use in reactors, and now it may be said that the power technology of plutonium is essentially handled in the traditional manner in the literature. Thus at the present time, essentially all of the information on plutonium, except that related to its use in weapons, is being published in all countries in the traditional manner, as it is being obtained. We can, therefore, look forward to finding the continuing story of plutonium in such publications.

The plutonium story is a continuing one. The fact that the concern here has been in the main with the wartime work accounts in part for the fact that our story has covered mainly American contributions, and even among these it has been necessary within the scope of this short review to omit the mention of many people who made significant contributions. The continuing development is involving many contributions from laboratories in all parts of the world. It seems clear that this element will continue to play an important role in the history of the world.

Chapter 2. Chemical Properties of the Actinide Elements

2.1 General Considerations

The chemical properties of nine transuranium elements are discussed in this chapter. These synthetic elements, with their chemical symbols and atomic numbers, can be listed as follows: neptunium, Np (93); plutonium, Pu (94); americium, Am (95); curium, Cm (96); berkelium, Bk (97); californium, Cf (98); einsteinium, E (99); fermium, Fm (100); and mendelevium, Mv (101). A great deal of information is available about their chemical properties, and, therefore, in a short summary such as this one, it is possible to discuss only a selected portion of this material.

It is more profitable to discuss their chemical properties in a correlative fashion, rather than element by element, because the presently known transuranium elements are all members of a chemical family, a transition series, similar to the series of rare earths running from lanthanum (number 57) to lutetium (number 71), known as the lanthanides and in which the 4*f* electron shell is filled. This second rare-earth series, the actinides (in which the 5*f* electron shell is filled) begins with actinium (number 89) and includes the natural elements thorium, protactinium, uranium, and the transuranium elements up through the undiscovered element 103. This concept that the heaviest elements are actinides has led to their placement in the periodic table as shown in Fig. 2.1. The positions which thorium, protactinium, and uranium have vacated, namely, the eka-hafnium, eka-tantalum, and eka-tungsten positions, will presumably be taken by the elements with atomic numbers 104, 105, and 106 when these are discovered.

1 H 1.0080																	2 He 4.003
3 Li 6.940	4 Be 9.013											5 B 10.82	6 C 12.011	7 N 14.008	8 O 16.000	9 F 19.00	10 Ne 20.183
11 Na 22.991	12 Mg 24.32											13 Al 26.98	14 Si 28.09	15 P 30.975	16 S 32.066	17 Cl 35.457	18 A 39.944
19 K 39.100	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.95	24 Cr 52.01	25 Mn 54.94	26 Fe 55.85	27 Co 58.94	28 Ni 58.71	29 Cu 63.54	30 Zn 65.38	31 Ga 69.72	32 Ge 72.60	33 As 74.91	34 Se 78.96	35 Br 79.916	36 Kr 83.80
37 Rb 85.48	38 Sr 87.63	39 Y 88.92	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.880	48 Cd 112.41	49 In 114.82	50 Sn 118.70	51 Sb 121.76	52 Te 127.61	53 I 126.91	54 Xe 131.30
55 Cs 132.91	56 Ba 137.36	57 La SEE La SERIES	72 Hf 178.50	73 Ta 180.95	74 W 183.86	75 Re 186.22	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.61	81 Tl 204.39	82 Pb 207.21	83 Bi 208.99	84 Po	85 At	86 Rn
87 Fr	88 Ra 226.03	89 Ac SEE Ac SERIES	(104)	(105)	(106)	(107)	(108)										

LANTHANIDE SERIES	57 La 138.92	58 Ce 140.13	59 Pr 140.92	60 Nd 144.27	61 Pm	62 Sm 150.35	63 Eu 152.0	64 Gd 157.26	65 Tb 158.93	66 Dy 162.51	67 Ho 164.94	68 Er 167.27	69 Tm 168.94	70 Yb 173.04	71 Lu 174.99
ACTINIDE SERIES	89 Ac 227.04	90 Th 232.05	91 Pa 231.05	92 U 238.04	93 Np 237.06	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 E	100 Fm	101 Mv	(102)	(103)

Fig. 2.1 Periodic table of the elements.

The transuranium elements are all of synthetic origin; hence their atomic weights, generally, depend on the source of the material, because this determines which isotopes are involved. The present information on the chemical properties of the heaviest transuranium elements is limited to that which has been obtained by working on the tracer scale of investigation. The isotopes which are suitable for the investigation of the transuranium elements in weighable amounts are listed in Table 2.1. It can be

TABLE 2.1 *Transuranium Nuclides Suitable for Investigations with Weighable Quantities*

ELEMENT	ISOTOPE	HALF LIFE
Neptunium	Np^{236}	>5000 y
	Np^{237}	2.20×10^6 y
Plutonium	Pu^{238}	86.4 y
	Pu^{239}	24,360 y
	Pu^{240}	6580 y
	Pu^{241}	13.0 y
	Pu^{242}	3.73×10^5 y
	Pu^{244}	7.6×10^7 y
Americium	Am^{241}	458 y
	Am^{242}	~ 100 y
	Am^{243}	7950 y
Curium	Cm^{242}	162.5 d
	Cm^{243}	35 y
	Cm^{244}	19 y
	Cm^{245}	1.4×10^4 y
	Cm^{246}	5000 y
	Cm^{247}	$\geq 4 \times 10^7$ y
	Cm^{248}	4.7×10^5 y
	Cm^{250}	2×10^4 y
Berkelium	Bk^{247}	7×10^3 y
	Bk^{249}	270 d
Californium	Cf^{249}	400 y
	Cf^{250}	9.3 y
	Cf^{251}	660 y
	Cf^{252}	2.2 y
Einsteinium	E^{254}	280 d

seen that suitable isotopes are available for each of the elements neptunium through einsteinium. Unfortunately, the present indications are that the study of the chemical properties of the elements

fermium (number 100) and above will always be limited to the use of the tracer method. The sources of Np^{237} and Pu^{239} were discussed in the first chapter, and the sources of most of the other isotopes listed in Table 2.1 will be described further in the next chapter.

With neptunium, the choice of isotope for use in chemical investigations is Np^{237}, which, because of its long half life, is relatively safe to work with and is available as a by-product in various chain reactors. Most of the work on plutonium to date has been done with the isotope Pu^{239}, which emits about 1.4×10^8 alpha particles per minute per milligram and requires great precautions in its handling. Although it has usually been mixed with varying amounts of the higher mass isotopes, the amounts have been so small that the specific alpha radioactivity has been essentially determined by the half life of the Pu^{239}. The isotopes Pu^{242}, and eventually Pu^{244}, are better for chemical investigations because of their longer half lives and lower specific activities.

Most of the investigations to date on the chemical properties of americium have been performed with the isotope Am^{241}. This isotope can be isolated in pure form from its parent 13.0-year, beta-emitting Pu^{241}, which is present in appreciable proportion in most reactor-produced plutonium. However, Am^{241} has a relatively high specific alpha radioactivity, emitting about 7×10^9 alpha particles per minute per milligram, and this makes it very difficult to handle. The isotope Am^{243}, which has a specific alpha activity some twenty times less, is produced in relatively high isotopic purity upon the intense neutron irradiation of plutonium due to the nature of the nuclear reactions and neutron-capture cross sections involved. Thus it is a particularly attractive isotope for use in the investigation of americium.

Much work on curium has been done using the isotope Cm^{242} which has a specific disintegration rate of 10^{13} alpha particles per minute per milligram. This makes its use almost prohibitively difficult, because of aggregate recoil of submicrogram particles and the rapid (radiation) decomposition of the water in its aqueous solutions. The isotope Cm^{244} has a specific alpha disintegration rate some forty times less and is formed relatively free of Cm^{242} as the result of the intense neutron irradiation of Pu^{239}. Thus Cm^{244}, and heavier isotopes, are available for the investigation of curium in

macroscopic quantities. The admixture of the heavier curium isotopes is the result of extremely high neutron irradiation of Cm^{244}; the specific alpha activity is reduced, thereby making such material most useful. The nature of the neutron-capture cross sections and the long half life combine to make the isotope Cm^{248} potentially the most useful of the curium isotopes for chemical studies.

The isotope Bk^{249} is suitable for the study of the chemical properties of berkelium with macroscopic amounts and is available as the result of intense neutron irradiation of lighter nuclides. The first isolation of berkelium in macroscopic amounts was accomplished by S. G. Thompson and B. B. Cunningham at Berkeley in April 1958. (The longer-lived Bk^{247} is not produced by neutron irradiation; hence it is not available in weighable amounts.) Californium has a number of isotopes suitable for investigations with weighable amounts. The isotope Cf^{249}, which, together with Cf^{251}, is one of the pair of the longest-lived isotopes, can be prepared in pure form through the beta decay of Bk^{249}. The element is also available as a mixture of Cf^{249}, Cf^{250}, Cf^{251}, and Cf^{252} (and shorter-lived isotopes) when the californium fraction is isolated after very intense neutron irradiation of Pu^{239} or of other elements of lower atomic number than californium. Fortunately the element einsteinium has the long-lived isomer E^{254} (280-day half life), making it possible to isolate this element in weighable amount. It, also, may be produced by the very intense neutron bombardment of plutonium or other elements lighter than einsteinium. Weighable amounts of berkelium, californium, and einsteinium are very difficult to handle because of their intense radioactivity, although some of the available isotopes of californium (e.g. Cf^{249}) are so long lived as to offer relatively less difficulty. The neutron emission from Cf^{252} presents a particularly difficult problem.

It is clear that the amounts of these elements available decrease markedly with increasing atomic number and that it is, therefore, very difficult to obtain einsteinium or fermium, and especially mendelevium.

2.2 The Metallic State

All of the actinide metals, like the lanthanide metals, are highly electropositive. They are produced by methods which are usual for the production of electropositive metals such as the electrolysis of fused salts, or, more often, by the reduction of a compound—for example, a halide like the fluoride—with an electropositive metal like calcium or barium. The known melting points, heats of vaporization and estimated boiling points, crystal-structure data for the various phases, and derived densities are listed in Table 2.2. Metallic protactinium, uranium, neptunium, and plutonium have complicated structures; americium is the first actinide to display a similarity to the lanthanide metals in its crystal structure. The metallic properties of plutonium are unique in that the properties of some of its allotropic modifications are not found in any other known metal. The interatomic distances deduced from crystal structure data indicate the presence of $6d$ electrons in these metals; however, from the standpoint of chemical reactivity they behave more like the lanthanide metals than like the metals of the $5d$ elements, such as tantalum, tungsten, rhenium, osmium, and iridium.

2.3 Oxidation States

Although the characteristic oxidation state of the actinides, like that of the lanthanides, is the III state, it does not become important until uranium, and the early elements in the series up to americium all display higher oxidation states in solution. This greater ease of oxidation of the actinide compared to the lanthanide elements is due to the lower relative binding energies of the $5f$ compared to the $4f$ electrons, a subject that will be discussed below. Thorium does not display a III state in aqueous solution at all, and the evidence for a III state in protactinium is scanty and at best indicates that it is a very unstable oxidation state. The higher oxidation states are of decreasing stability in proceeding up the series, so that when americium is reached, the III state is the only stable state in acidic aqueous solution. The III state is the only state that can exist in aqueous solution for curium. An especially interesting

TABLE 2.2 *Properties of Actinide Metals*[a]

ELEMENT	MELTING POINT (°C)	HEAT OF VAPORIZATION AND BOILING POINT	*Crystal Structure*						DENSITY	
			PHASE	RANGE OF STABILITY (°C)	SYMMETRY	LATTICE PARAMETERS, A a_0	b_0	c_0	g/cm³	Temp. (°C)
Actinium	1100 ± 50	(70 kcal/mole)			F.C. cubic	5.311				
Thorium	1750	130–177 kcal/mole; (3000–4200°C)								
			α	R.T.–1400	F.C. cubic	5.086			11.724	25
			β	1400–1750	B.C. cubic	4.11				
Protactinium	(<1873)				Tetragonal	3.925		3.238	15.37	
Uranium	1132	106.7 kcal/mole (3818°C)								
			α	R.T.–668	Orthorhombic	2.8541	5.8692	4.9563	19.04	25
			β	668–774	Tetragonal	10.759		5.656	18.11	720
			γ	774–1132	B.C. cubic	3.525			18.06	805
Neptunium	640									
			α	R.T.–278	Orthorhombic	4.723	4.887	6.663	20.45	25
			β	278–570	Tetragonal	4.897		3.338	19.36	313
			(γ	570–640	Cubic	3.52			18.00	600)
Plutonium	639.5	80.46 ± 0.34 kcal/mole (3235°C)								
			α	R.T.–122	Monoclinic	6.1835	4.8244	10.973	19.737	25
			β	122–203					17.77	150
			γ	203–317	Orthorhombic	3.1603	5.7624	10.141	17.19	210
			δ	317–453	F.C. cubic	4.6370			15.92	320
			δ'	453–477	Tetragonal	4.701	c/a = 0.955	4.489	15.99	465
			ϵ	477–640	B.C. cubic	3.638			16.48	500
Americium	below 900° C	57 kcal/mole (2607°C)	α	R.T.–75	Hexagonal	3.642		11.76	11.87	

[a] Estimated and uncertain quantities in parentheses.

point is the existence of a water-stable IV state, in addition to the III state, in the next element, berkelium, a reflection of the fact that berkelium has eight 5*f* electrons, one more than the stable structure corresponding to the half-full shell. It seems quite possible that the next element, californium, might similarly reflect the stability of the half-filled 5*f* shell by exhibiting an attainable V state (presumably CfO_2^+).

The known oxidation states of the actinide and lanthanide elements are summarized in Table 2.3 in such a way as to bring out

TABLE 2.3 *Oxidation States of Actinide and Lanthanide Elements*

LANTHANIDE ELEMENTS:										
Atomic number	57	58	59	60	61	62	63	64	65	66
Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy
Oxidation states						2	2			
	3	3	3	3	3	3	3	3	3	3
		4	(4)						(4)	
ACTINIDE ELEMENTS:										
Atomic number	89	90	91	92	93	94	95	96	97	98
Element	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf
Oxidation states	3	(3)	(3)	3	3	3	3	3	3	3
		4	4	4	4	4	(4)	(4)	4	
			5	5	5	5	5			
				6	6	6	6			

the analogy between the two groups and to show the greater ease of oxidation for members of the actinide family. The oxidation states which are very unstable toward oxidation or reduction, as the case may be, are designated with parentheses; none of these latter states can exist in aqueous solution but have been produced only in solid compounds—although protactinium (III) may be an exception. The IV state of curium is limited to solid CmO_2 and CmF_4, showing the strong tendency of curium to retain the III oxidation state with the stable half-filled 5*f* electronic shell. The oxidation states of the actinide elements in Table 2.3 are underlined in such a way as to show the variation in their stability in going across the series.

The increasing stability of the lower oxidation states, in particular the III state, in going up the actinide series of elements, is

well illustrated by a consideration of the solid halides. Table 2.4, which lists all of the halides of the elements from actinium to curium that have been prepared as stable compounds in the solid state, points up this increasing stability of the lower oxidation states. In this table, parentheses enclose the formulas for compounds whose existence, although probable, has not been unequivocally characterized.

One of the most interesting correlations of properties in the actinides is the uniformity of ionic types and the similarity in chemical properties of corresponding ionic types in the group. There are four cationic types in acidic aqueous solution: M^{+3}, M^{+4}, MO_2^+, and MO_2^{++}. Each of these is remarkably similar in behavior from one actinide to another; although, of course, the oxidation-reduction relationships and hence the relative stabilities differ markedly from element to element. The MO_2^+ and MO_2^{++} type ions have remarkable stability with respect to their binding of oxygen atoms and are almost unique among the ions of all the known elements. These ionic groups persist through a great variety of chemical changes and behave as single entities with properties somewhat intermediate between singly or doubly charged ions and ions of similar size but of somewhat higher charge. The existence of so many cations introduces some very interesting complexities into the aqueous-solution chemistry of a number of the actinides.

TABLE 2.5 *Ion Types and Colors for Actinide Ions*

ELEMENT	M^{+3}	M^{+4}	MO_2^+	MO_2^{++}
Actinium	colorless	—	—	—
Thorium	—	colorless	—	—
Protactinium	—	colorless	(colorless)	—
Uranium	red	green	(color unknown)	yellow
Neptunium	blue to purple	yellow-green	green	pink to red
Plutonium	blue to violet	tan to orange-brown	(reddish purple)	yellow to pink-orange
Americium	pink	—	yellow	rum-colored
Curium	colorless	—	—	—

Table 2.5 lists the ion types, designated with their known characteristic colors, which can exist in aqueous solution for each of the

TABLE 2.4 *Halides of the Actinide Elements*

ELEMENT	FLUORIDES				CHLORIDES				BROMIDES		IODIDES	
Ac				AcF_3				$AcCl_3$		$AcBr_3$		(AcI_3)
Th			ThF_4				$ThCl_4$		$ThBr_4$		ThI_4	
Pa		(PaF_5)	PaF_4			$(PaCl_5)$	$PaCl_4$		$(PaBr_5)$		(PaI_5)	
U	UF_6	UF_5	UF_4	UF_3	UCl_6	UCl_5	UCl_4	UCl_3	UBr_4	UBr_3	UI_4	UI_3
Np	NpF_6		NpF_4	NpF_3			$NpCl_4$	$NpCl_3$	$NpBr_4$	$NpBr_3$		NpI_3
Pu	PuF_6		PuF_4	PuF_3				$PuCl_3$		$PuBr_3$		PuI_3
Am			AmF_4	AmF_3				$AmCl_3$		$AmBr_3$		AmI_3
Cm			CmF_4	CmF_3								

actinide elements. The open spaces indicate that the corresponding oxidation states do not exist in aqueous solution. The color of plutonium (V) has not been observed but is deduced from the absorption spectrum of its aqueous solution. In the case of protactinium, it seems unlikely that protactinium (V) exists as PaO_2^+, and the status of protactinium (III) in aqueous solution is pretty much unknown. Such a wide and rich variety of colors is, of course, characteristic of a transition series of elements. These colors are so

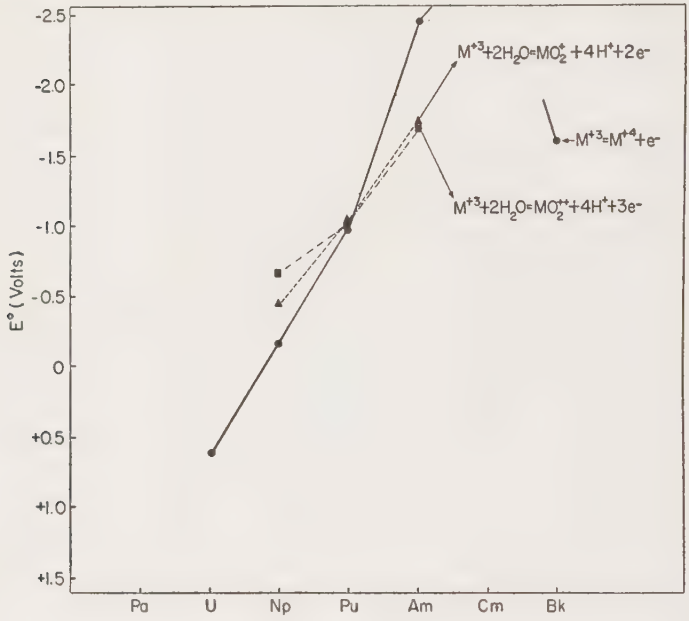


Fig. 2.3 Aqueous formal oxidation potentials of the actinide ions for the III-IV, III-V, and III-VI couples.

interesting that a mere listing in a table cannot do them justice, and therefore a color picture, furnished through the courtesy of G. W. Parker of the Oak Ridge National Laboratory, is reproduced in Fig. 2.2. The colors of the ions in solution depend, of course, on the concentrations and upon the other ions present, hence the colors reproduced in this figure can only be approximations representing somewhat average conditions.

The oxidation-reduction relationships in the actinide elements

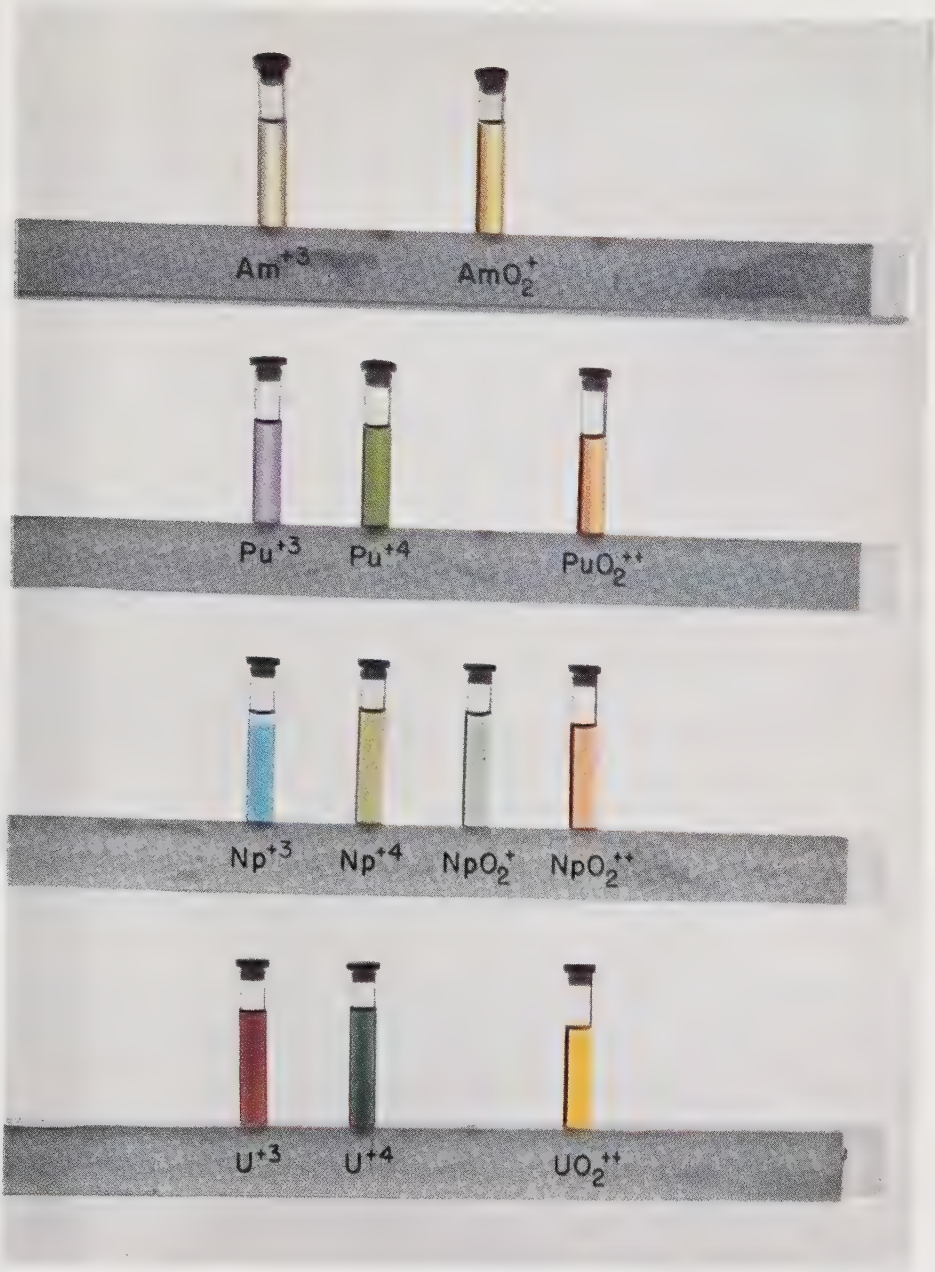


Fig. 2.2 Color of Actinide Ions. Photograph furnished by G. W. Parker of the Oak Ridge National Laboratory.

TABLE 2.6 *Formal Oxidation Potentials of the Actinide Elements*[a]

ELEMENT	OXIDATION POTENTIALS (VOLTS)						
	$M—M^{+3}$ 0–III	$M^{+3}—M^{+4}$ III–IV	$M^{+3}—MO_2^+$ III–V	$M^{+3}—MO_2^{++}$ III–VI	$M^{+4}—MO_2^+$ IV–V	$M^{+4}—MO_2^{++}$ IV–VI	$MO_2^+—MO_2^{++}$ V–VI
Actinium	(∼2.6)						
Thorium	1.90[b]						
Protactinium	(∼1.0)[c]				(+0.1)		
Uranium	1.80	+0.631			−0.58	−0.32	−0.063
Neptunium	1.83	−0.155	−0.447	−0.677	−0.739	−0.938	−1.137
Plutonium	2.03	−0.9818		−1.0228	−1.1721	−1.0433	−0.9133
Americium	2.32	−2.44	−1.74	−1.69	−1.04		−1.60
Curium	—						
Berkelium		−(1.6)					

[a] Estimated values given in parenthesis.

[b] Value for Th $(s) \rightarrow Th^{+4}$ (aq).

[c] Value for the reaction $Pa + 2H_2O \rightarrow PaO_2^+ + 4H^+$.

are summarized in the form of the formal potentials in Table 2.6, and the potentials are plotted in Figs. 2.3 and 2.4 in such a way as to bring out their variation with atomic number. These are the "formal potentials," defined as the measured potentials corrected to unit concentrations of the substances entering into the reactions, on the basis of the hydrogen-hydrogen-ion couple taken as zero volts, and with no corrections for activity coefficients. Cell measurements,

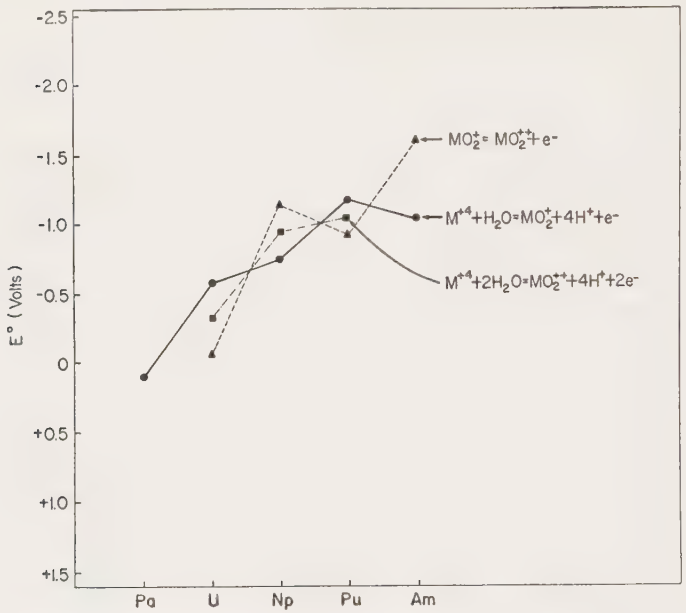


Fig. 2.4 Aqueous formal oxidation potentials of the actinide ions for the IV-V, IV-VI, and V-VI couples.

equilibrium measurements, and heat-of-reaction measurements have been used to establish these potentials. The measurements which are summarized in Table 2.6 have been generally made in solutions of 1 *M* perchloric acid. The M^{+3}—M^{+4} and the MO_2^+—MO_2^{++} couples are readily reversible and can be measured with cells, facts which are to be correlated with the one-electron changes involving no making or breaking of bonds. The M^{+3}—MO_2^+, M^{+3}—MO_2^{++}, M^{+4}—MO_2^+, and M^{+4}—MO_2^{++} couples are not revers-

ible, presumably because of slowness introduced in the making and breaking of oxygen bonds, and, therefore, these potentials are not amenable to direct cell measurements. The increasing difficulty of oxidation above the III state with increasing atomic number is apparent. The curve for the $M^{+3} \rightarrow M^{+4}$ change is interesting in that it shows a regular increase in potential from uranium to

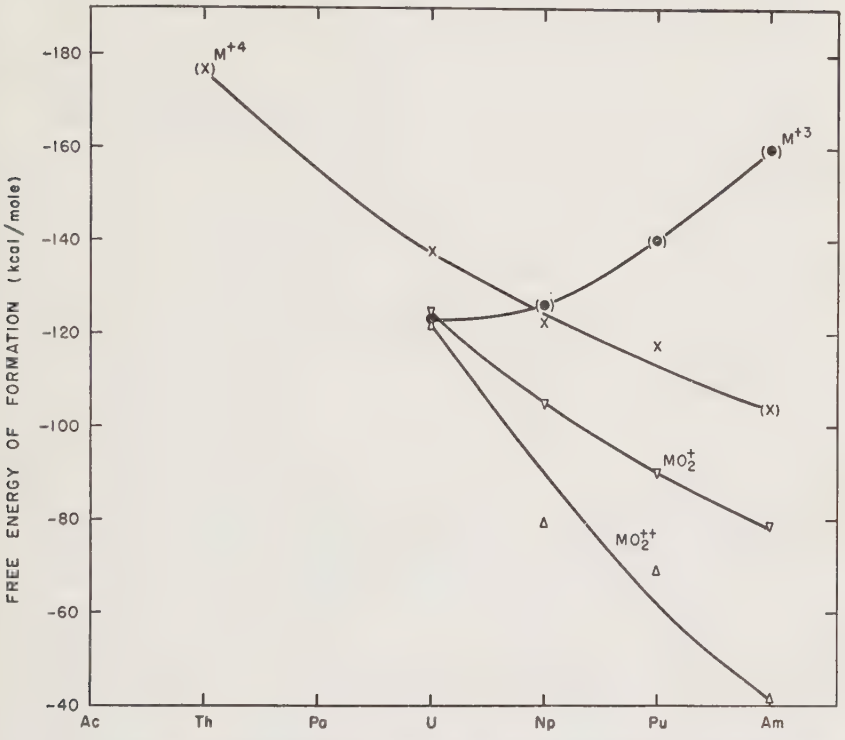
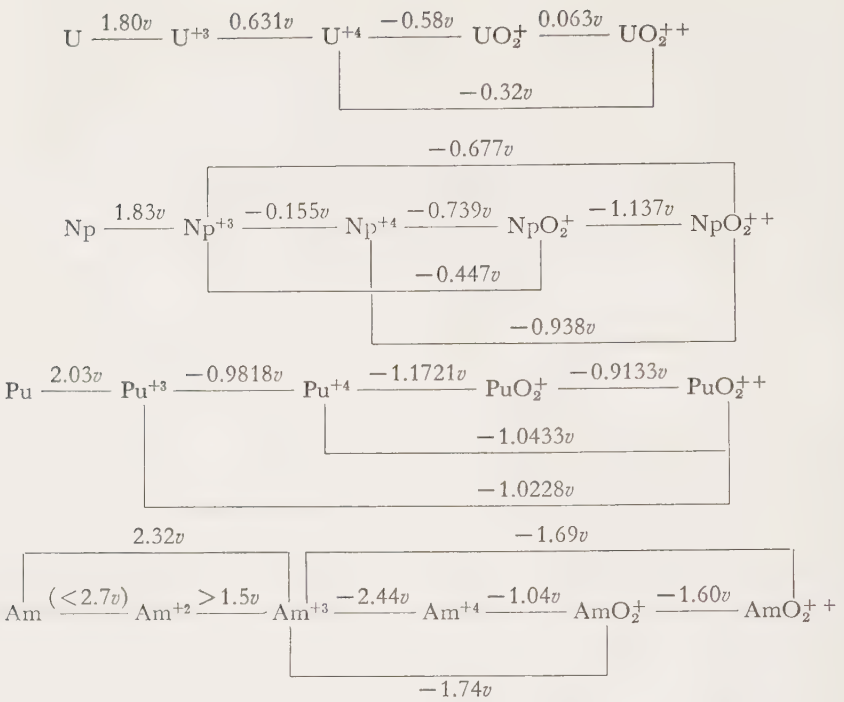


Fig. 2.5 Free energy of formation of actinide ions. (Minus $2\Delta f_{H_2O(l)}$ for MO_2^+ and MO_2^{++}.)

curium with a drop at berkelium (reflecting the half-filled 5*f* shell), and presumably the curve will rise again after berkelium. The free energies of formation of the ions are summarized in Fig. 2.5.

The potential relationships for the elements with multiple oxidation states are especially interesting and can best be considered on the basis of the following potential diagrams:



These couples, of course, determine the equilibrium conditions and whether a given reagent is capable of effecting oxidation or reduction of one of these oxidation states. In addition, some generalizations can be made about the rates and the kinetics of such oxidation-reduction reactions. The oxidation of M^{+3} to M^{+4} or of MO_2^+ to MO_2^{++}, or the reverse reactions, as one-electron reactions involving no formation or breaking of bonds as far as the actinides are concerned, are rapid with other one-electron reducing or oxidizing agents that involve no bond changes (such as the ferrous-ferric couple), and the rate varies from fast to slow with reagents that normally react by two-electron or bond-breaking changes. In the cases of the other actinide couples, oxidation or reduction requires the making or breaking of bonds with oxygen, so the rates of reaction are limited by the slowness of the actinide couples and are decreased by any further slowness introduced by the reducing or oxidizing agents.

These potentials are such as to lead to a number of dispropor-

tionation reactions. Thus the ions which undergo appreciable disproportionation in dilute-acid solution are UO_2^+ (to U^{+4} and UO_2^{++}), Pu^{+4} (to Pu^{+3} and PuO_2^{++}), PuO_2^+ (to Pu^{+4} and PuO_2^{++}) and AmO_2^+ (to Am^{+3} and AmO_2^{++}). The equilibria are such that UO_2^+, PuO_2^+, and AmO_2^+ can ordinarily exist only at very low concentrations, and the optimum conditions are at low acidities just short of the point where hydrolysis reactions set in; the kinetics for these disproportionation reactions are very complicated and have been studied in some detail. The potentials are such that NpO_2^+ is stable and is, therefore, one of the most important neptunium ionic species (together with Np^{+4} and NpO_2^{++}). The situation for plutonium is especially complex and is discussed in the following paragraph. The most important uranium ions in aqueous solution are U^{+4} and UO_2^{++}, while Am^{+3} is the most important aqueous americium ion. The most important oxidation state for thorium is obviously Th^{+4}; for protactinium, the protactinium (V) state of uncertain formula; and for the remainder of the actinide elements, the M^{+3} state, with an additional M^{+4} state of some importance for berkelium.

The oxidation states of plutonium deserve some special discussion, because the oxidation-reduction relationships are about the most intricate known to chemistry. The proximity to each other of the oxidation-reduction potentials in acidic solution signifies that appreciable amounts of three or four oxidation states can exist together at equilibrium. The most important equilibrium is that represented by the reaction:

$$3\ \text{Pu (IV)} = 2\ \text{Pu (III)} + \text{Pu (VI)}.$$

For example, in 0.5 *M* HCl at 25°C the equilibrium percentages of plutonium in the various oxidation states are found to be 27.2 per cent Pu (III), 58.4 per cent Pu (IV), 13.6 per cent Pu (VI)—and 0.75 per cent Pu (V). The net reaction is believed to correspond to:

$$3\ Pu^{+4} + 2\ H_2O = 2\ Pu^{+3} + PuO_2^{++} + 4\ H^+,$$

showing the great effect of variation of acidity. Another equilibrium, important at low acidity where PuO_2^+ can exist in appreciable concentration, is represented by the reaction:

$$\text{Pu (V)} + \text{Pu (IV)} = \text{Pu (VI)} + \text{Pu (III)}.$$

For 0.1 *M* perchloric acid at 25°C the value of K defined by

$$K = \frac{[Pu\ (VI)][Pu\ (III)]}{[Pu\ (V)][Pu\ (IV)]}$$

has been found to be 10.7, illustrating the existence of appreciable concentrations of all four ionic species. The reaction apparently may be written as:

$$Pu^{+4} + PuO_2^+ = PuO_2^{++} + Pu^{+3},$$

indicating the absence of any acidity effect on the equilibrium. Equilibrium is established rapidly, since only electron transfer and no breaking of plutonium-oxygen bonds is involved. Under conditions where this equilibrium involving four oxidation states is established rapidly, the equilibrium

$$3\ Pu\ (IV) = 2\ Pu\ (III) + Pu\ (VI)$$

is established only slowly because this involves the breaking of plutonium-oxygen bonds. Thus the rather striking condition can exist in which all four of the oxidation states are in equilibrium with respect to one reaction, whereas three oxidation states are not in equilibrium with respect to another reaction. The complexity of the oxidation-reduction relationships is further illustrated by a consideration of the disproportionation mechanisms of PuO_2^+ and Pu^{+4}, which are slow reactions due to the breaking of plutonium-oxygen bonds. Both disproportionations apparently involve the reaction:

$$Pu\ (IV) + Pu\ (IV) \rightleftarrows Pu\ (III) + Pu\ (V). \qquad (1)$$

At low concentrations of Pu (III) the disproportionation of Pu (V) apparently proceeds through the reaction:

$$Pu\ (V) + Pu\ (V) \rightleftarrows Pu\ (IV) + Pu\ (VI). \qquad (2)$$

However, in the presence of Pu (III), which may appear, for example, as the product of the oxidation of Pu (V) by Pu (IV), reaction 1, proceeding as written to the left, becomes the rate-determining step. The mechanism for the disproportionation of Pu (IV) also apparently involves reaction 1 proceeding as written to the right, with the additional rapid oxidation of Pu (V) to Pu (VI) by Pu (IV).

The oxidation-reduction potentials of the actinide elements in

alkaline solutions are also of interest. The values in 1 M sodium hydroxide may be summarized in the following diagrams:

$$\mathrm{Th} \xrightarrow{2.48v} \mathrm{Th(OH)_4}$$

$$\mathrm{U} \xrightarrow{2.17v} \mathrm{U(OH)_3} \xrightarrow{2.14v} \mathrm{U(OH)_4} \xrightarrow{0.62v} \mathrm{UO_2(OH)_2}$$

$$\mathrm{Np} \xrightarrow{2.25v} \mathrm{Np(OH)_3} \xrightarrow{1.76v} \mathrm{Np(OH)_4} \xrightarrow{-0.39v} \mathrm{NpO_2OH} \xrightarrow{-0.48v} \mathrm{NpO_2(OH)_2}$$

$$\mathrm{Pu(OH)_3 \cdot xH_2O} \xrightarrow{0.95v} \mathrm{Pu(OH)_4 \cdot yH_2O} \xrightarrow{-0.76v} \mathrm{PuO_2(OH)_{aq}} \xrightarrow{-0.26v} \mathrm{PuO_2(OH)_3^-{}_{aq}}$$

$$\sim -0.5v$$

$$\mathrm{Am} \xrightarrow{2.71v} \mathrm{Am(OH)_3} \xrightarrow{0.4v} \mathrm{Am(OH)_4} \xrightarrow{(-0.7v)} \mathrm{AmO_2OH} \xrightarrow{(-1.1v)} \mathrm{AmO_2(OH)_2}$$

The stability of the various actinide ions in aqueous solution with respect to oxidation and reduction has been depicted in a useful way by H. A. C. McKay and J. Milsted. Table 2.7 is based on their summary.

2.4 Hydrolysis and Complex Ions

The order of decreasing degree of hydrolysis or complex-ion formation is as follows: $M^{+4} > MO_2^{++} > M^{+3} > MO_2^{+}$. The actinide ions form somewhat stronger complex ions than the corresponding lanthanide ions. The relatively high tendency toward hydrolysis and complex-ion formation of the MO_2^{++} type ion, in spite of the fact that it has a charge of only two, is presumably connected with a high concentration of charge on the metal atom. It might be expected, on the basis of the increasing charge and decreasing size of the ion (see below) that the degree of hydrolysis, for each ion type, should increase with increasing atomic number. The available data indicate that starting at some point in the group, generally at about uranium, for each ion type a regularity of hydrolytic properties is observed which is of the type expected for a rare-earth-like series. However, for two of the ion types, MO_2^{+} and MO_2^{++}, the degree of hydrolysis decreases with increasing atomic number, indicating the operation of more complicated factors than simple charge and size. The second and third hydrolysis constants, differences in the cation formal charge due to variation in the extent of covalency of the M-O bonds, and possible differences in

TABLE 2.7 *Stability of Actinide Ions in Aqueous Solution*

ION	STABILITY
U^{+3}	Aqueous solutions evolve hydrogen on standing.
Np^{+3}	Stable to water, but readily oxidized by air to Np^{+4}.
Pu^{+3}	Stable to water and air, but easily oxidized to Pu^{+4}; oxidizes slightly under the action of its own alpha radiation.
Am^{+3}	Stable; difficult to oxidize.
Cm^{+3}	Stable.
Bk^{+3}	Stable; can be oxidized to Bk^{+4}.
Cf^{+3}	Stable.
E^{+3}	Stable.
Fm^{+3}	Stable.
Mv^{+3}	Stable.
U^{+4}	Stable to water, but slowly oxidized by air to UO_2^{++}.
Np^{+4}	Stable to water, but slowly oxidized by air to NpO_2^{+}.
Pu^{+4}	Stable in concentrated acid, e.g., 6 *M* HNO_3, but disproportionates to Pu^{+3} and PuO_2^{++} at lower acidities.
Am^{+4}	Not known in solution.
Cm^{+4}	Not known in solution.
Bk^{+4}	Stable; easily reduced to Bk^{+3}.
UO_2^{+}	Disproportionates to U^{+4} and UO_2^{++}; most stable at pH 2–4.
NpO_2^{+}	Stable; disproportionates only at high acidities.
PuO_2^{+}	Always tends to disproportionate; most stable at very low acidities.
AmO_2^{+}	Disproportionates in strong acid; reduces fairly rapidly under the action of its own alpha radiation at low acidities (in form of Am^{241}).
UO_2^{++}	Stable; difficult to reduce.
NpO_2^{++}	Stable; easy to reduce.
PuO_2^{++}	Stable; fairly easy to reduce; reduces slowly under the action of its own alpha radiation (in form of Pu^{239}).
AmO_2^{++}	Reduces fairly rapidly under the action of its own alpha radiation (in form of Am^{241}).

the structures of polynuclear types and polymeric species will all have to be considered.

Polymeric species are known to be of importance in the hydrolysis of actinide ions, and polymeric plutonium (IV) is of special interest. A brilliant green color is developed upon heating a dilute hydrochloric- or nitric-acid solution of plutonium (IV). This polymerized plutonium, which can also be developed in other ways, can take the form of a positive colloid, subject to adsorption on a

number of surfaces, and the molecular weight and particle size can be varied as the result of various treatments.

Hydrolysis is of overwhelming importance in the chemistry of protactinium in the important V state. In fact, this feature is so troublesome as to make the chemistry of protactinium notoriously difficult. Protactinium (V) must be held in solution by a complexing ion such as fluoride ion; it is to be hoped that protactinium (IV) ion, which is moderately stable in aqueous solution, will give a means to handle protactinium more successfully in aqueous solution.

There are a large number of qualitative and a few quantitative data available on complex-ion formation in the actinide elements. The relative tendency toward complex-ion formation is, in general, controlled to a large extent by the factors of ionic size and charge. As mentioned above, the stability of the complex formed with a given anion decreases, in general, in the order $M^{+4} > MO_2^{++} > M^{+3} > MO_2^{+}$. Although there is some variation within each of these actinide ionic types, the order of complexing power of different anions is, in general, in the order fluoride > nitrate > chloride > perchlorate for mononegative anions and in the order carbonate > oxalate > sulfate for dinegative anions. The formation of anion complexes is of special importance in connection with ion exchange and solvent-extraction behavior. Elution from cation exchange resins (see below), adsorption on anion exchange resins, and extraction into organic solvents depends on the formation of complex ions. A large number of complex ions are formed with organic substances.

Thus the formation of complex ions explains the important organic-solvent extraction properties of the actinide elements. The types of solvents which show high extraction for specific oxidation states of the actinides are TBP, diethyl ether, ketones such as diisopropyl ketone or methyl isobutyl ketone, and several glycol-ether-type solvents such as diethyl cellosolve or dibutyl carbitol. Solvent extraction is usually carried out in nitrate systems because very strongly complexing anions are to be avoided, and some organic solvents, such as diethyl ether or methyl isobutyl ketone require a high concentration of nitrate ion in the aqueous phase if

extraction of the actinide elements is to occur. The extractability of the actinide-element ions changes somewhat from element to element and depends markedly on the oxidation state. In general the extractability increases in the order $PuO_2^{++} < NpO_2^{++} < UO_2^{++}$ for these VI state ions. The V state is generally extracted rather poorly, but very little data are available except for protactinium, which is a complicated case. Although the actinide elements in the IV oxidation state can be extracted to some extent into the solvents such as the ketones, which are very efficient for the extraction of the VI oxidation state, a better solvent for the IV state is TBP, usually diluted to a 20-volume per cent solution with some other organic solvent such as carbon tetrachloride, benzene, *n*-butyl ether, or kerosene, and with a high concentration of nitrate in the aqueous phase; the extractability generally increases in the order Th (IV) < Np (IV) < Pu (IV). The tripositive actinide ions have low extractability into these organic solvents, although they can be extracted into TBP when the concentration of nitric acid in the aqueous phase is very high. This difference in extractability of the tripositive and tetrapositive actinide ions can be the basis for a rapid and quantitative separation of certain ions; for example, the ratio of the distribution coefficient for berkelium (IV) to the distribution coefficients for berkelium (III) and curium (III) is about 10^6 for extraction into di(2-ethyl hexyl) ortho-phosphoric acid–heptane from aqueous nitric acid. In summary, the extraction of the actinide-element ions from aqueous nitrate systems into TBP increases in the order: hexapositive ions (high extractability), Pu (VI) < Np (VI) < U (VI); pentapositive ions (very low extractability); tetrapositive ions (high extractability), Th (IV) < Np (IV) < Pu (IV); tripositive ions (low extractability), Pu (III) < Am (III) < Cm (III); plutonium ions, Pu (III) $\ll$ Pu (VI) < Pu (IV). These properties make it possible to devise solvent extraction procedures for the separation of the actinide elements from each other, and from other elements, by utilizing either the differences in extraction coefficients for actinide ions of a given oxidation state or the gross variation in extractability of different oxidation states.

A number of organic compounds are known which form compounds with aqueous actinide ions that can be extracted from aque-

ous solution into immiscible organic solvents. These include the acetylacetone complexes and compounds with reagents such as cupferron (the ammonium salt of nitrosophenylhydroxylamine) with the IV state actinides. The chelate complexes are of special interest, and, among these, the ones formed with diketones such as TTA have proved very effective in a number of separation procedures involving the III and IV oxidation states.

2.5 Solid Compounds

The precipitation properties of the actinide M^{+3} ions are similar to those of the tripositive lanthanide ions and those of M^{+4} to those of Ce^{+4}. Thus the fluorides and oxalates are insoluble in acid solution, whereas the nitrates, halides, sulfates, perchlorates, and sulfides are all soluble. The M^{+4} ions are precipitated by iodate and various substituted arsenates even from rather strongly acid solutions. The MO_2^+ actinide ions may be precipitated as the potassium salt from strong carbonate solutions. The MO_2^{++} ion separates as the beautifully crystalline salt $NaMO_2(CH_3COO)_3$ from solutions containing a high concentration of sodium and acetate ions, a highly characteristic reaction for this ionic type. The hydroxides of all four ionic types are insoluble and are formed by hydrolysis reactions as mentioned above; in the case of the MO_2^{++} ions, precipitation can occur from alkaline solution to form compounds of the type illustrated by sodium diuranate ($Na_2U_2O_7$). The addition of peroxide to solutions containing actinide ions, particularly the M^{+4} ions, leads to the formation of complex peroxy compounds in solution and the precipitation of such compounds even from solutions of moderate acidity, often with the incorporation of inorganic anions (such as sulfate, nitrate or chloride).

A number of solid compounds of the actinide elements together with crystal structure and some other properties are summarized in Table 2.8. These compounds can be prepared by more or less standard preparative techniques for inorganic compounds. These are often modified in the direction of microchemical methods because of the small amounts of material available or the extreme intensity of radioactivity of the material which not only is a health hazard but may cause rapid destruction of the crystalline lattice by

TABLE 2.8 *Properties and Crystal Structure Data for Some Important Actinide Compounds*

COMPOUND	COLOR	MELTING POINT (°C)	Crystal Structure: SYMMETRY	SPACE GROUP OR STRUCTURE TYPE	LATTICE PARAMETERS, A: a_0	b_0	c_0	DENSITY (g/cc)
ThH_2	Black		Tetragonal		4.10		5.03	9.20
Th_4H_{15}	Black		Cubic		9.11			
PaH_3	Black		Cubic		6.648			
β-UH_3	Black		Cubic		6.6310			10.92
Np_2H_{15}	Black							
PuH_2	Black		Cubic	Fm3m				10.40
PuH_3	Black		Hexagonal	$P6_3/mmc$	3.78		6.76	9.61
AmH_2	Black		Cubic					
Am_4H_{15}	Black		Cubic					
Ac_2O_3	White		Hexagonal	La_2O_3	4.07		6.29	9.19
Pu_2O_3			Hexagonal	La_2O_3	3.841		5.958	11.47
Am_2O_3	Tan		Hexagonal	La_2O_3	3.817		5.971	11.77
	Reddish brown		Cubic	Mn_2O_3	11.03			10.57
Cm_2O_3	White		Cubic		5.50			
ThO_2	White	~3050	Cubic	Fluorite	5.5859			10.00
PaO_2	Black		Cubic	Fluorite	5.505			
UO_2	Brown to black	2800 ± 200	Cubic	Fluorite	5.648			10.97
NpO_2	Apple green		Cubic	Fluorite	5.425			11.11
PuO_2	Yellow green to brown	~1750	Cubic	Fluorite	5.3960			11.46
AmO_2	Black		Cubic	Fluorite	5.383			11.68
CmO_2	Black		Cubic	Fluorite	5.372			
AcF_3	White		Hexagonal	LaF_3	4.17		7.53	7.88
UF_3	Black	>1140 (dec.)	Hexagonal	LaF_3	4.146		7.348	8.95
NpF_3	Purple or black		Hexagonal	LaF_3	4.108		7.273	9.12
PuF_3	Purple	1425	Hexagonal	LaF_3	4.087		7.240	9.32
AmF_3	Pink		Hexagonal	LaF_3	4.067		7.225	9.53
CmF_3			Hexagonal	LaF_3				
$AcCl_3$	White		Hexagonal	UCl_3	7.62		4.55	4.81
UCl_3	Red	835	Hexagonal	$C6_3/m$	7.442		4.320	5.51

TABLE 2.8 *Properties and Crystal Structure Data for Some Important Actinide Compounds (Continued)*

COMPOUND	COLOR	MELTING POINT (°C)	Crystal Structure					DENSITY (g/cc)
			SYMMETRY	SPACE GROUP OR STRUCTURE TYPE	LATTICE PARAMETERS, A			
					a_0	b_0	c_0	
$NpCl_3$	White	~800	Hexagonal	$C6_3/m$	7.405		4.273	5.58
$PuCl_3$	Emerald green	760	Hexagonal	$C6_3/m$	7.380		4.238	5.70
$AmCl_3$	Pink		Hexagonal	$C6_3/m$	7.38		4.25	5.78
$AcBr_3$	White		Hexagonal	$C6_3/m$	8.06		4.68	5.85
UBr_3	Red	730	Hexagonal	$C6_3/m$	7.942		4.440	6.53
α-$NpBr_3$	Green		Hexagonal	$C6_3/m$	7.917		4.382	6.62
β-$NpBr_3$	Green		Orthorhombic	Ccmm	12.65	4.11	9.15	6.62
$PuBr_3$	Green	681	Orthorhombic	Ccmm	12.62	4.09	9.13	6.69
$AmBr_3$	White		Orthorhombic	Ccmm	12.6	4.11	9.12	
ThF_4	White	1111	Monoclinic	UF_4	13.1	11.01 $\alpha_2 = 126 \pm 1°$	8.6	5.71
PaF_4	Reddish brown		Monoclinic	UF_4				
UF_4	Green	960	Monoclinic	C2/c	12.82	10.74 $\alpha_2 = 126°10'$	8.41	6.70
NpF_4	Green		Monoclinic	UF_4	12.67	10.62 $\alpha_2 = 126°10'$	8.31	6.8
PuF_4	Brown	1037	Monoclinic	UF_4	12.59	10.55 $\alpha_2 = 126°10'$	8.26	7.0
AmF_4	Tan		Monoclinic	UF_4	12.49	10.47 $\alpha_2 = 126°10'$	8.19	
CmF_4			Monoclinic	UF_4				
$ThCl_4$	White	770	Tetragonal	I4/amd	8.473		7.468	4.60
$PaCl_4$	Greenish yellow		Tetragonal	I4/amd	8.377		7.482	
UCl_4	Green	590	Tetragonal	I4/amd	8.296		7.487	4.87
$NpCl_4$	Red-brown	538	Tetragonal	I4/amd	8.25		7.46	4.92
UF_6	White	64.02/1137 mm	Orthorhombic	Pnma	9.900	8.966	5.207	5.060
NpF_6	Brown	53	Orthorhombic	Pnma	9.91	8.97	5.21	5.00
PuF_6	Reddish brown	50.75	Orthorhombic					

displacing atoms from their normal lattice sites as the result of collisions with alpha particles or recoiling nuclei. Thus the hydrides are formed as the result of the reaction of the metals with hydrogen; the subsequent decomposition of a hydride by heating leads to the production of finely divided metal, which is useful as the starting point for the synthesis of many other compounds. The oxides can be formed by the reaction of the metals with oxygen or by the decomposition of an oxygen-containing compound such as a hydroxide, nitrate, or oxalate; the use of hydrogen or excess oxygen often determines whether a lower or higher oxide is formed. For the elements with multiple oxidation states, the actinide-oxygen systems are very complex, and many phases with variable composition are observed; thus for a given element (like uranium, or americium) the composition can show a continuous variation with changes in temperature and pressure of oxygen, and several phase changes as the ratio of oxygen to actinide element is changed from the lowest to the highest values corresponding to stable compounds.

The lower fluorides are usually prepared by the action of hydrogen fluoride (and in some cases hydrogen) on the oxides, while the higher fluorides are generally prepared with the additional use of fluorine or oxygen. The chlorides can be made by direct combination of chlorine with the metal or hydride, by hydrochlorination of oxides, or by chlorination of oxides with carbon tetrachloride, phosgene, sulfur chloride, bromine trichloride, or other powerful chlorinating agents; a lower form such as uranium trichloride may require the use of hydrogen as a reducing agent. The bromides may be formed by direct combination of bromine with the metal or hydride or by hydrobromination of oxides. The synthesis of the iodides is usually best accomplished by direct combination of the elements or by the reaction of the metal with hydrogen iodide. Except for the trifluorides the halides are so hygroscopic as to require handling in an anhydrous atmosphere. With the heavier halogens it is particularly easy to form the oxyhalides through the action of water vapor. The higher halides are quite volatile, and even the trihalides are appreciably volatile at moderately elevated temperatures, so that all except the trifluorides may be readily purified by sublimation in high vacuum.

The actinide elements form compounds with many elements

TABLE 2.9 *Ionic Radii of Actinide and Lanthanide Elements*

NO. OF 4*f* OR 5*f* ELECTRONS	*Lanthanide Series*				*Actinide Series*			
	ELEMENT	RADIUS (Å)	ELEMENT	RADIUS (Å)	ELEMENT	RADIUS (Å)	ELEMENT	RADIUS (Å)
0	La^{+3}	1.061			Ac^{+3}	1.11	Th^{+4}	0.99
1	Ce^{+3}	1.034	Ce^{+4}	0.92	(Th^{+3})	(1.08)	Pa^{+4}	0.96
2	Pr^{+3}	1.013	Pr^{+4}	0.90	(Pa^{+3})	(1.05)	U^{+4}	0.93
3	Nd^{+3}	0.995			U^{+3}	1.03	Np^{+4}	0.92
4	Pm^{+3}	(0.979)			Np^{+3}	1.01	Pu^{+4}	0.90
5	Sm^{+3}	0.964			Pu^{+3}	1.00	Am^{+4}	0.89
6	Eu^{+3}	0.950			Am^{+3}	0.99		
7	Gd^{+3}	0.938						
8	Tb^{+3}	0.923	Tb^{+4}	0.84				
9	Dy^{+3}	0.908						
10	Ho^{+3}	0.894						
11	Er^{+3}	0.881						
12	Tm^{+3}	0.869						
13	Yb^{+3}	0.858						
14	Lu^{+3}	0.848						

which are not listed in the brief compilation given in Table 2.8. The binary compounds with carbon, nitrogen, silicon, and sulfur are of especial interest because of their general refractory character and stability at high temperatures.

Crystal-structure data have led to the derived ionic radii which are summarized in Table 2.9 and plotted in Fig. 2.6. It will be noticed that there is an *actinide contraction* for both the M^{+3} and M^{+4} ions, analogous to the *lanthanide contraction*, as the positive charge

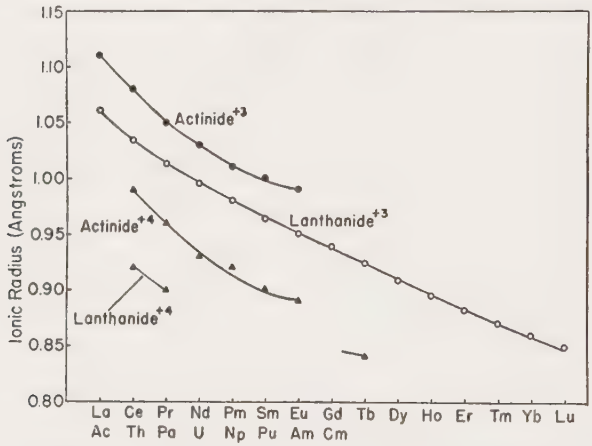


Fig. 2.6 Ionic radii of lanthanide and actinide ions.

on the nucleus increases. This, of course, is a consequence of the addition of successive electrons to an inner electron shell, the 5*f* shell, so that the imperfect screening of the increasing nuclear charge by additional *f* electrons results in a contraction of the outer or valence orbit. An important fact is that analogous compounds are generally isostructural, a consequence of the ionic nature of most actinide compounds and the similarity of the ionic radii for a given oxidation state. In some cases (e.g. UBr_3-$NpBr_3$-$PuBr_3$-$AmBr_3$) there is a change in structure type, proceeding up the group, which is consistent with the contraction which takes place. The special stability of the (fluorite) MO_2 structure is noteworthy, leading to such compounds as PaO_2, AmO_2, and CmO_2 despite the instability of the first and the nonexistence of the latter two elements in the IV oxidation state in aqueous solution. The contraction and the

isostructural properties of the compounds constitute some of the best evidence for the transition character of this group of elements.

2.6 Absorption and Fluorescence Spectra

2.6a Aqueous Absorption Spectra

The absorption spectra of the actinide ions, as do those of the lanthanide ions, contain narrow bands in the visible, near-ultraviolet, and near-infrared regions of the spectrum. These spectra are less influenced by chemical environment than are the spectra of the *d*-electron transition group ions. Many lines of evidence show that the narrow absorption bands in the lanthanides and actinides are to be ascribed to electronic transitions within the $4f$ and $5f$ shells, in which the $4f^n$ and $5f^n$ configurations are preserved in the upper and lower states for a particular ion. Although dipole radiation is forbidden in such a situation by the La Porte rule, there are various mechanisms involving electrostatic–crystalline-field and configurational interactions which cause a partial breakdown of the rule and make forbidden transitions possible. In general, the absorption bands of the actinide ions are a factor of some ten times more intense than those of the lanthanide ions. This is due in part to the decreased shielding of $5f$ electrons, which increases their susceptibility to perturbations by crystalline fields. The absorption bands are observed in both the aqueous ions and in crystals.

The complexity of the absorption spectra corresponding to these transitions within the $5f$ shell, over the entire range of wave lengths, is directly related to the number of terms arising from a particular electron configuration. In principle, neglecting crystal-field splitting and spin-orbit coupling effects, the number of bands observed should equal the number of excited-state terms for a particular configuration. The possible configurations and the number of their terms (in parentheses) are given in the following list: $f \sim f^{13}$ (1); $f^2 \sim f^{12}$ (7); $f^3 \sim f^{11}$ (17); $f^4 \sim f^{10}$ (47); $f^5 \sim f^9$ (73); $f^6 \sim f^8$ (119); f^7 (117). Experimentally, there does appear to be a general increase in complexity of the spectra in going from the ends of the series toward the middle. Actually it is difficult to construct energy-level diagrams from the data which are available, although this should eventually be possible. Two points should be particularly stressed.

First, the spectra involving only one *f* electron are especially simple, since they consist of the single transition $^2F_{5/2} \leftrightarrow {}^2F_{7/2}$. The second point is that for the configuration f^7 (half-filled shell) found in gadolinium and curium, the lowest-lying excited state is much higher above the ground state than is the case for the other lanthanide and actinide elements with unfilled *f* electron shells. The spectra of Gd^{+3} and Cm^{+3} are, therefore, confined to the ultraviolet region of the spectrum.

The ultraviolet absorption-spectra for U^{+3}, Np^{+3}, Pu^{+3}, and Am^{+3} are broad and show an interesting progression toward the ultraviolet with increasing atomic number. These are apparently due to $5f \rightarrow 6d$ transitions and indicate that this energy difference increases with atomic number, in agreement with the atomic spectroscopic data discussed below, Section 2.7.

2.6b Absorption and Fluorescence in Crystals

The sharpest absorption, corresponding to transitions within the 5*f* shell, occurs in crystals. Some of these absorption "lines," for example in americium, are only a few angstroms wide. Fluorescence is generally observed in actinide compounds under proper conditions for excitation. For example, fluorescence can be excited in the trichlorides of uranium, neptunium, plutonium, americium, and curium, diluted with lanthanum chloride, through the action of ultraviolet light. Thus it is possible in principle through the use of absorption and fluorescence data to construct electronic energy-level diagrams for a number of actinide ions in the crystalline state and to correlate these with the gaseous atomic spectroscopy data on the energy levels for various electronic configurations.

2.7 Electronic Structure

Table 2.10 presents what appears to be the configuration or the best prediction for the configuration (beyond the radon structure) of the ground state of the neutral gaseous atom for each of the elements from actinium to element 103. The configurations of actinium, thorium, uranium and americium are known as the result of the analysis of spectroscopic data obtained in connection with the measurement of the emission lines from the neutral and charged

TABLE 2.10 *Suggested Electron Configurations for Gaseous Atoms of Actinide and Lanthanide Elements*

ATOMIC NUMBER	ELEMENT	ELECTRON CONFIGURATION[a] AND TERM SYMBOL	ATOMIC NUMBER	ELEMENT	ELECTRON CONFIGURATION[b] AND TERM SYMBOL
89	Actinium	$6d7s^2$ ($^2D_{3/2}$)	57	Lanthanum	$5d6s^2$ ($^2D_{3/2}$)
90	Thorium	$6d^27s^2$ ($^3F_2$)	58	Cerium	$4f^26s^2$ ($^3H_4$)
91	Protactinium	$5f^26d7s^2$ ($^4K_{11/2}$)	59	Praseodymium	$4f^36s^2$ ($^4I_{9/2}$)
92	Uranium	$5f^36d7s^2$ ($^5L_6$)	60	Neodymium	$4f^46s^2$ ($^5I_4$)
93	Neptunium	$5f^46d7s^2$ ($^6L_{11/2}$)	61	Promethium	$4f^56s^2$ ($^6H_{5/2}$)
94	Plutonium	$5f^67s^2$ ($^7F_0$)	62	Samarium	$4f^66s^2$ ($^7F_0$)
95	Americium	$5f^77s^2$ ($^8S_{7/2}$)	63	Europium	$4f^76s^2$ ($^8S_{7/2}$)
96	Curium	$5f^76d7s^2$ ($^9D_2$)	64	Gadolinium	$4f^75d6s^2$ ($^9D_2$)
97	Berkelium	$5f^86d7s^2$ ($^8H_{17/2}$) or $5f^97s^2$ ($^6H_{15/2}$)	65	Terbium	$4f^96s^2$ ($^6H_{15/2}$)
			66	Dysprosium	$4f^{10}6s^2$ ($^5I_8$)
98	Californium	$5f^{10}7s^2$ ($^5I_8$)	67	Holmium	$4f^{11}6s^2$ ($^4I_{15/2}$)
99	Einsteinium	$5f^{11}7s^2$ ($^4I_{15/2}$)	68	Erbium	$4f^{12}6s^2$ ($^3H_6$)
100	Fermium	$5f^{12}7s^2$ ($^3H_6$)	69	Thulium	$4f^{13}6s^2$ ($^2F_{7/2}$)
101	Mendelevium	$5f^{13}7s^2$ ($^2F_{7/2}$)	70	Ytterbium	$4f^{14}6s^2$ ($^1S_0$)
102		$5f^{14}7s^2$ ($^1S_0$)	71	Lutetium	$4f^{14}5d6s^2$ ($^2D_{5/2}$)
103		$5f^{14}6d7s^2$ ($^2D_{5/2}$)			

[a] Beyond radon. The indicated term symbols are those for pure Russell-Saunders coupling, while the true structure is better described by the assumption that $5f$ and $6d$ electrons are separately in Russell-Saunders coupling and are weakly coupled to one another. The configurations for all elements beyond curium are predicted ones.

[b] Beyond xenon.

gaseous atoms. The protactinium, neptunium, plutonium and curium electronic structures were obtained from atomic beam experiments. The trend in the spectroscopic, paramagnetic susceptibility, paramagnetic resonance, atomic beam, light absorption, chemical, and other properties, with their implications that the 5*f* becomes progressively of lower energy compared to the 6*d* level as the atomic number increases, has been used as an aid in making the predictions. Spectroscopic and atomic beam data have also given much information about the electronic configurations and positions of levels above the ground states for a number of the elements. The configurations (beyond xenon) of the corresponding neutral lanthanide elements are also given in Table 2.10 for comparison.

Much is known about the electronic configurations of the aqueous actinide ions and of actinide compounds. Measurements of paramagnetic susceptibility, paramagnetic resonance, light absorption, and crystal structure, as well as a consideration of the chemical and other properties, have given this information. In general, all of the electrons beyond the radon core in the actinide compounds and in aqueous actinide ions are in the 5*f* shell. (There are a few exceptions such as U_2S_3 and subnormal compounds such as Th_2S_3 where 6*d* electrons are present.)

In the case of a few compounds of some of the early elements in the series, the energy necessary for a shift between the 5*f* and 6*d* shells is within the range of chemical binding energies. Since the energy difference between such far outlying levels as the 5*f* and 6*d* shells is rather small, and since configurational mixing (between states of the same parity) should be rather large, these may be predominant factors in determining that a composite energy-level lies lowest. Much of the experimental data covered earlier, such as the ease of oxidation to higher states, points to lower binding and less electrostatic shielding by outer electrons of 5*f* compared to 4*f* electrons, just as should be expected, and the magnitude of these effects seems reasonable. It should also be pointed out that the configuration of the gaseous atom may not correspond to that of the compounds or that of the hydrated ions in solution. In fact, in the case of the lanthanides, the configuration of the gaseous atom has, in general, only two electrons (beyond the xenon structure) outside the 4*f* shell, although the predominant oxidation state is certainly

the III state. It is in some of the compounds of the elements thorium, protactinium, and uranium that the relative energy position of the 5*f* and 6*d* levels is most uncertain. As in the other transition series, the relative energy position of the shell which is undergoing the filling process becomes lower as the successive electrons are added, and, by the time neptunium, plutonium, and the subsequent members of the series are reached, the 5*f* shell seems clearly to be definitely of lower energy than the 6*d* shell.

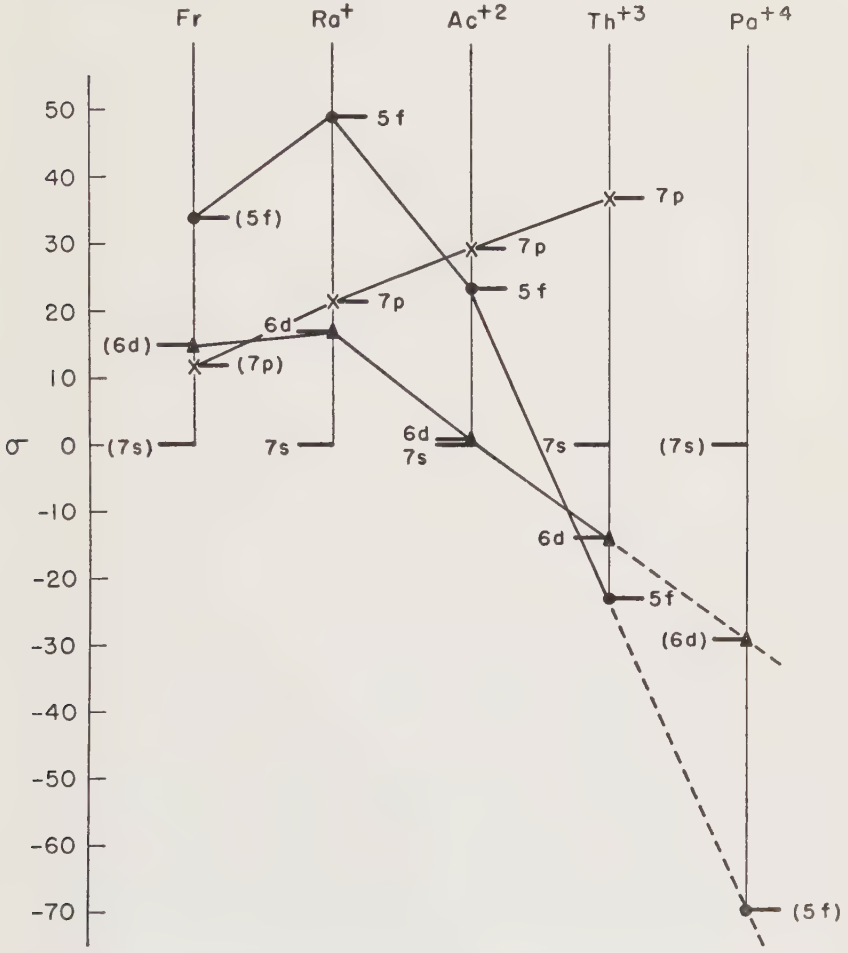


Fig. 2.7 Relative binding energies in francium isoelectronic sequence. (Term values, σ, in 10^3 cm^{-1}.)

The spectroscopic data are sufficient to make it possible to estimate the relative binding energies for the 5*f*, 6*d*, 7*s*, and 7*p* electrons. This has been done by M. S. Fred, with the results as plotted in Figs. 2.7, 2.8, and 2.9 for the energies of the 5*f*, 6*d*, and 7*p* electrons relative to the 7*s* electrons for various isoelectronic se-

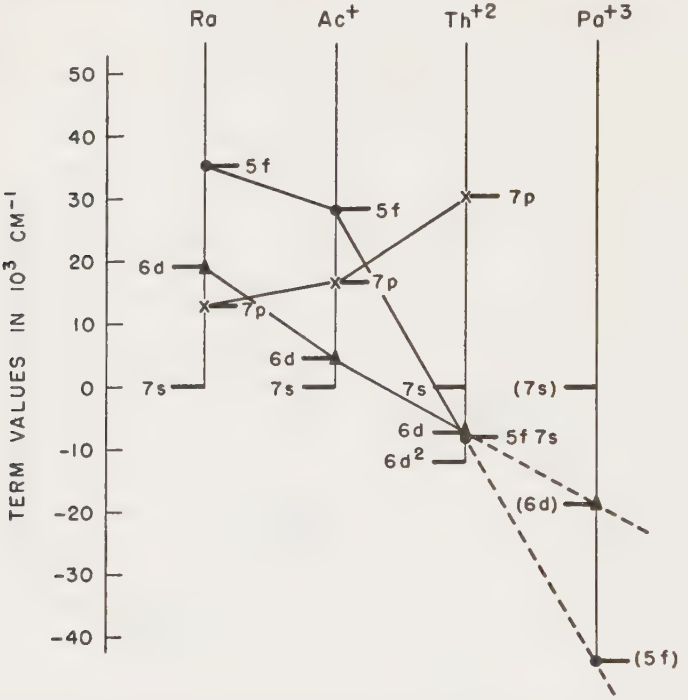


Fig. 2.8 Relative binding energies in the radium isoelectronic sequence.

quences. The energies in Figs. 2.8 and 2.9 are obtained by differences and are therefore very approximate. (For example, in the case of Th^+ in Fig. 2.9 the 7*s*-7*p* energy difference can be obtained from the energy difference between $6d^27s$ and $6d^27p$ or between $6d7s^2$ and $6d7s7p$, which give similar but not identical results.) It may be noted that the relative binding energy of the 5*f* electron increases with atomic number and net charge on the ion, both of which are increasing in the plots. In Fig. 2.10 the relative stability of the 5*f* electron is shown to increase with atomic number for constant single charge on the ion. In Table 2.11 is listed the energy in cm^{-1},

similarly determined, needed to convert a 7*s* electron to a 5*f*, 6*d*, or 7*p* electron. The numbers in italics are the energies, while the intermediate numbers are the differences in energies from which the individual effects of increasing atomic number and increasing charge on the ion can be determined. It is clear that the relative

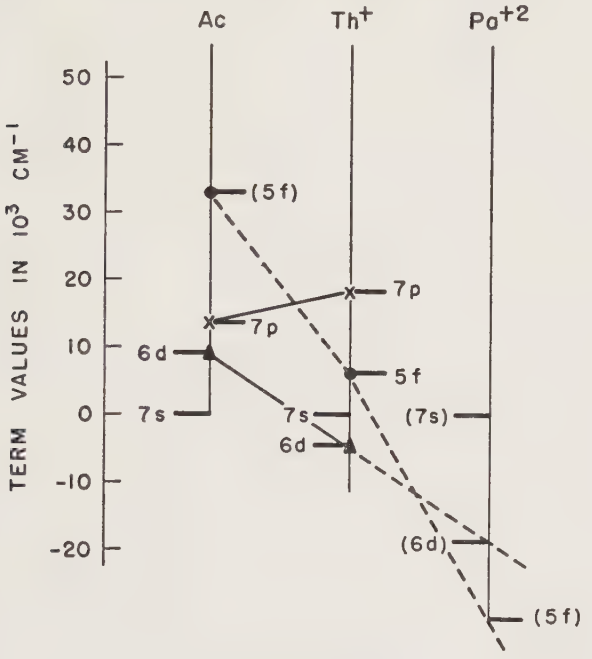


Fig. 2.9 Relative binding energies in actinium isoelectronic sequence.

stability of the 5*f* electrons increases in comparable amount with both increasing atomic number and ionic charge in this region.

Of special interest for the interpretation of the chemical behavior of the heavy elements is the relative binding energies of the 5*f* and 6*d* electrons as a function of atomic number and net charge as shown in Table 2.12. The values in parentheses are extrapolations from the known spectroscopic data, while the value in italics is inferred from the positions of the strong aqueous solution absorption bands assumed to be due to $5f^n \rightarrow 5f^{n-1}d$ transitions and is seen to be in approximate agreement with the corresponding extrapolated value. The corresponding 4*f*-5*d* separations are shown in

Table 2.13. Although these data are taken from atomic spectroscopy, the evidence is that this is a somewhat quantitative manifestation of the same sort of situation which exists with the aqueous ions and compounds of these elements. The relative binding of the 5*f* compared to 6*d* electrons increases with increasing atomic number and ionic charge. However, the increase in binding energy of

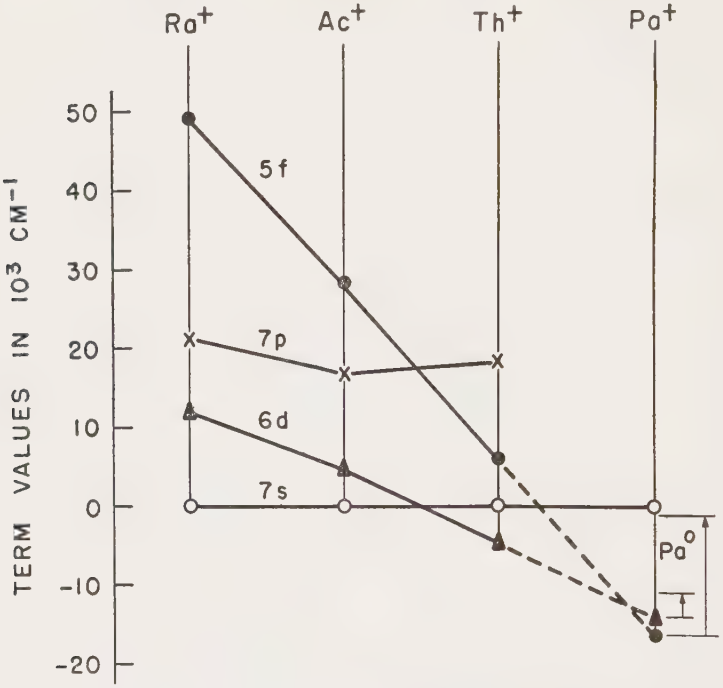


Fig. 2.10 Relative binding energies of singly charged ions.

the 5*f* electrons is not so large as with 4*f* electrons, accounting for the greater tendency for higher oxidation states in the actinide elements. The 6*d* and 5*f* electrons have comparable binding energies near the beginning of the series. The 6*d* electrons are especially favored in the subnormal oxidation states near the beginning of the series, in agreement with the experimental data for such compounds as Th_2S_3 and U_2S_3 where 6*d* electrons are found. Also in agreement with this favoring of the 6*d* electrons in the lowest oxidation states is the fact that the zero, or metallic, state of a number of the early actinide elements contains 6*d* electrons.

TABLE 2.11 *Binding Energies of 5f, 6d, and 7p Relative to 7s Electrons* (cm^{-1})

		88		*89*		*90*	*92*	*95*
	M	*35255*						*−2722*
		13733						−3557
	M^+	*48988*	−20787	*28201*	−22033	*6168*		*−6279*
5f				−4746		−14075		
	M^{+2}			*23455*	−31362	*−7907*		
						−15223		
	M^{+3}					*−23130*		
	M	*19152*	−9935	*9217*				*15136*?
		−7068		−4477				−914
	M^+	*12084*	−7344	*4740*	−9301	*−4561*	*289*	*14222*?
6d				−3939		−2776		
	M^{+2}			*801*	−8138	*−7337*		
						−6600		
	M^{+3}					*−13937*		
	M	*13078*	635	*13713*			*17969*	*15608*
		8273		2979			231	
	M^+	*21351*	−4659	*16692*	1522	*18214*	*18200*	
7p				12774		12084		
	M^{+2}			*29466*	832	*30298*		
						684		
	M^{+3}					*37109*		

The comparable binding energy of the 5*f*-, 6*d*-, 7*p*- and 7*s*-levels for a range of several atomic numbers is a favorable condition for the use of these orbitals in hybridized bonds. The greater spatial extension and slower shrinkage of the 5*f* relative to the 4*f* orbitals make the 5*f* orbitals more available for such hybridization closer to the atomic number where the levels start to fill, rather than

TABLE 2.12 *Relative Binding Energies of 5f and 6d Electrons* (cm^{-1})

Z	M	M^+	M^{+2}	M^{+3}	M^{+4}
87	(18989)				
88	16103	36904			
89	(24000)	23461	22654		
90	(18000)	10729	−570	−9193	
91		(−2000)	(−12000)	(−25000)	(−40000)
					−36000
95	−17858	−20501			

TABLE 2.13 *Relative Binding Energies of 4f and 5d Electrons* (cm^{-1})

Z	M	M^+	M^{+2}	M^{+3}	M^{+4}
55	9973				
56	17159	43386			
57	21207	12754			
58		~−5000	−37163	−49737	
				−40000	
63	−27852	−30189			

several atomic numbers earlier as is apparently the case for the 4*f* orbitals. Thus hybridization involving 5*f* orbitals seems to account for the greater tendency for covalent complex-ion formation of the actinide as compared to the lanthanide elements. Some bond types involving symmetrical arrangements as given by J. C. Eisenstein are summarized in Table 2.14. The strengths of the *f* hybrid orbitals are

TABLE 2.14 *The Strengths of Some Hybrid Orbitals*

NO. OF BONDS	ORBITALS USED	ANGULAR DISTRIBUTION OF BONDS	STRENGTH
2	sp	linear	1.932
2	sf	linear	2.578
2	df	linear	3.452
3	p^3	mutually perpendicular	1.732
3	f^3	mutually perpendicular	2.646
4	sp^3	tetrahedral	2.000
4	sf^3	tetrahedral	2.028
4	sp^2d	square	2.694
4	sf^2d	square	3.280
6	d^2sp^3	octahedral	2.923
6	d^2sf^3	octahedral	3.570

taken to be the maximum values of the hybrid wave functions, ignoring the radial parts of the hybridized orbitals. In addition to the predominantly covalent bonds involving *f* orbitals, there is probably an *f* covalent contribution to many bonds in ionic compounds. Also it is worth commenting on certain variations in the stability of anionic complexes of the actinide ions in going across the series, which, for example, lead to the reversal of elution positions from ion exchange resins as mentioned in the following section. These variations may in some cases be related to the minimum in

the ligand field stabilization which occurs in a transition series for cations in an *S* ground state, as in curium, as pointed out by C. K. Jørgensen.

2.8 Ion Exchange Behavior

One of the most striking chemical features of the actinides is their behavior in ion exchange resin adsorption and elution experiments, where a great similarity between the tripositive actinides and lanthanides is observed. This important process has been the key to the discovery of all of the actinide elements beyond curium, making it possible to predict with accuracy the crucial chemical properties to be utilized for identification purposes in the discovery experiments. This will be illustrated later in this chapter (Sections 2.8a and 2.8b) by showing in some detail how the use of such chemical methods led to the discovery of berkelium, californium, einsteinium, and fermium, the elements with atomic numbers 97 to 100 inclusive. Therefore, this will also serve as an historical account of the discovery of these elements. This account will be preceded by a general discussion of the ion exchange and elution properties of the actinide elements.

All four oxidation states may be adsorbed by (i.e. made to undergo exchange with) cation exchange resins such as Dowex-50 (a copolymer of styrene and divinylbenzene with nuclear sulfonic acid functional groups) and Amberlite (a copolymer of formaldehyde and phenol with carboxylic and phenolic functional groups). The actinide ions can, in general, be desorbed by elution with such ions as chloride, nitrate, sulfate, and especially citrate, lactate, alpha-hydroxyisobutyrate, and ethylene diamine tetraacetate. The elution order depends on a balance between the degree of adherence to the resin and the strength of the complex ion formed with the eluting agent and is often in the inverse order of the atomic number. The formation of negatively charged complex ions with anions permits adsorption and elution from anionic exchange resins such as Dowex-1 (a copolymer of styrene and divinyl benzene with quaternary ammonium groups) and Amberlite IRA-400 (a quaternary ammonium polystyrene), and the order of elution is often the reverse of that from the cationic exchange resins.

The order of elution of the various oxidation states relative to each other is so dependent on the particular resin and eluting agent used that no generalization of the behavior is possible. For a given oxidation state, very little information with respect to dependence on atomic number is available except for the III oxidation state. Therefore, the following summary will depend on the description of a number of interesting particular situations.

The M^{+3} ions can be separated easily from each other by elution through cation exchange columns using solutions of certain organic anions as eluants. Therefore, such systems have been the subject of many investigations. The organic eluants in most common use are lactic acid and alpha-hydroxyisobutyric acid. In both cases the reactive grouping is $—C(OH)\cdot COO^-$. And in both cases, the elution proceeds in inverse order of atomic number for the lanthanide as well as the actinide series. The spacings between the actinide M^{+3} ions show many similarities with those exhibited by their homologues in the lanthanide series, thus emphasizing the close similarity in chemical behavior of the two series. The ion Th^{+4} elutes with alpha-hydroxyisobutyric acid a little earlier than Mv^{+3}. Pu^{+4} is usually extensively hydrolyzed under the conditions used, but it elutes as a broad band in approximately the position of Cf^{+3}.

The M^{+3} ions of the actinide series are more strongly complexed by the chloride ion than are the corresponding lanthanide ions. Group separation methods which make use of this behavior have therefore been devised. From Dowex-50 cation resin with saturated hydrochloric acid ($\sim$13 *M*), the actinide +3 ions elute much faster than the lanthanide ions. From Dowex-1 anion resin, the reverse is true. To obtain very high activities of chloride ion, solutions of lithium chloride are often used. Members of both series can then be complexed as negative ions which are strongly retained by Dowex-1 anion resin and eluted as concentrated chloride solution continues to pass through the resin.

The elution order of the actinide ions from Dowex-50 resin by hydrochloric acid shows interesting variations with concentration of the eluant. In acid concentrations up to about 6 *M* the M^{+3} actinide ions elute in inverse order of atomic number. In saturated hydrochloric acid containing 20 per cent ethyl alcohol, the order

is Fm^{+3}, E^{+3}, Cf^{+3}, Bk^{+3}, Am^{+3}, and Cm^{+3}. Note that the order of Cm^{+3} and Am^{+3} is reversed.

Chloride systems with Dowex-1 anion resin are frequently used for separation procedures. Unless the chloride ion activity is very high, the M^{+3} actinide ions and Th^{+4} are not retained appreciably by the resin. UO_2^{++}, Pu^{+4}, and Np^{+4}, however, are strongly retained. UO_2^{++} may be eluted rapidly with 1 *M* hydrochloric acid. Pu^{+4} and Np^{+4} are usually eluted with hydrochloric acid of about 6 *M* containing a reducing agent such as hydroxylamine or iodide ion which reduces them to the M^{+3} state.

In solutions with high chloride ion activity, such as 13 *M* hydrochloric acid, the elution order of the actinide M^{+3} ions from Dowex-1 anion resin is Am^{+3} and Cm^{+3} together; Bk^{+3}; Cf^{+3} and E^{+3} together; Fm^{+3}. The Cm^{+3} and Am^{+3} elute very rapidly.

Elution with ammonium-thiocyanate solution from Dowex-1 anion resin may be used to obtain a group separation between the actinide and lanthanide M^{+3} ions, since the lanthanides elute more rapidly than any of the actinides. In elution with 1 *M* ammonium thiocyanate, the elution sequence is Cm^{+3}, Am^{+3}, E^{+3}, Bk^{+3} and Fm^{+3} together, Cf^{+3}. The order is, therefore, rather unusual.

Systems involving Dowex-1 anion resin and nitric-acid eluant have interesting possibilities for separation procedures. The M^{+3} ions are not strongly retained by the resin, nor is UO_2^{++}. Th^{+4} and Pu^{+4}, however, are strongly adsorbed from 8 *M* nitric acid and may thus be separated from the M^{+3} ions.

The details of the various elution sequences are not well understood. A summary of part of the experimental information is shown in Fig. 2.11. That there are certain irregularities, such as points of inflection at curium and californium, is obvious from a study of this figure. It seems probable that a full understanding of such effects would require a more intimate knowledge of the nature of the chemical binding in the various complex ions than is at present available. Bond hybridization, possibly using 5*f* orbitals, hydration, Stark and steric effects, and the minimum in ligand field stabilization (mentioned above) may be involved in addition to simple considerations of ionic size and charge.

In the adsorption-elution method for the identification of new

actinide elements, the family resemblance between the tripositive actinide and lanthanide elements is taken advantage of through the use of regular elution sequences and simple apparatus. All of the elements present in the tripositive oxidation state in a mixture

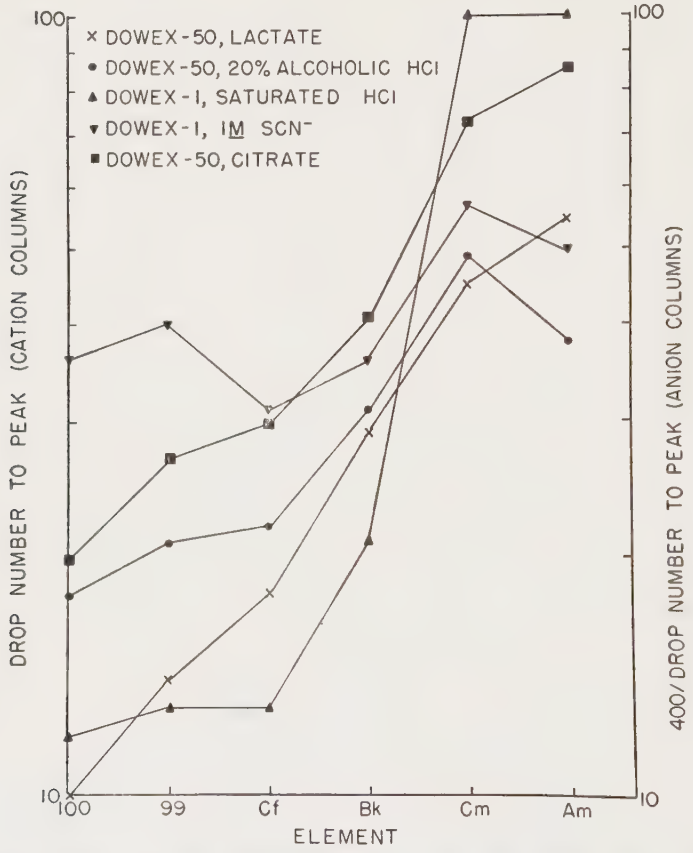


Fig. 2.11 Summary of elution positions of the elements from americium to fermium for various types of ion exchange columns and eluants. (After Thompson, Harvey, Choppin, and the author.)

of actinides and/or lanthanides can be placed in simple chemical combination with the organic polymer (or resin) which has the exchangeable cations. The tripositive actinide or lanthanide ions in aqueous solution undergo the simple chemical exchange when the solid organic polymer is stirred into the solution. This solid

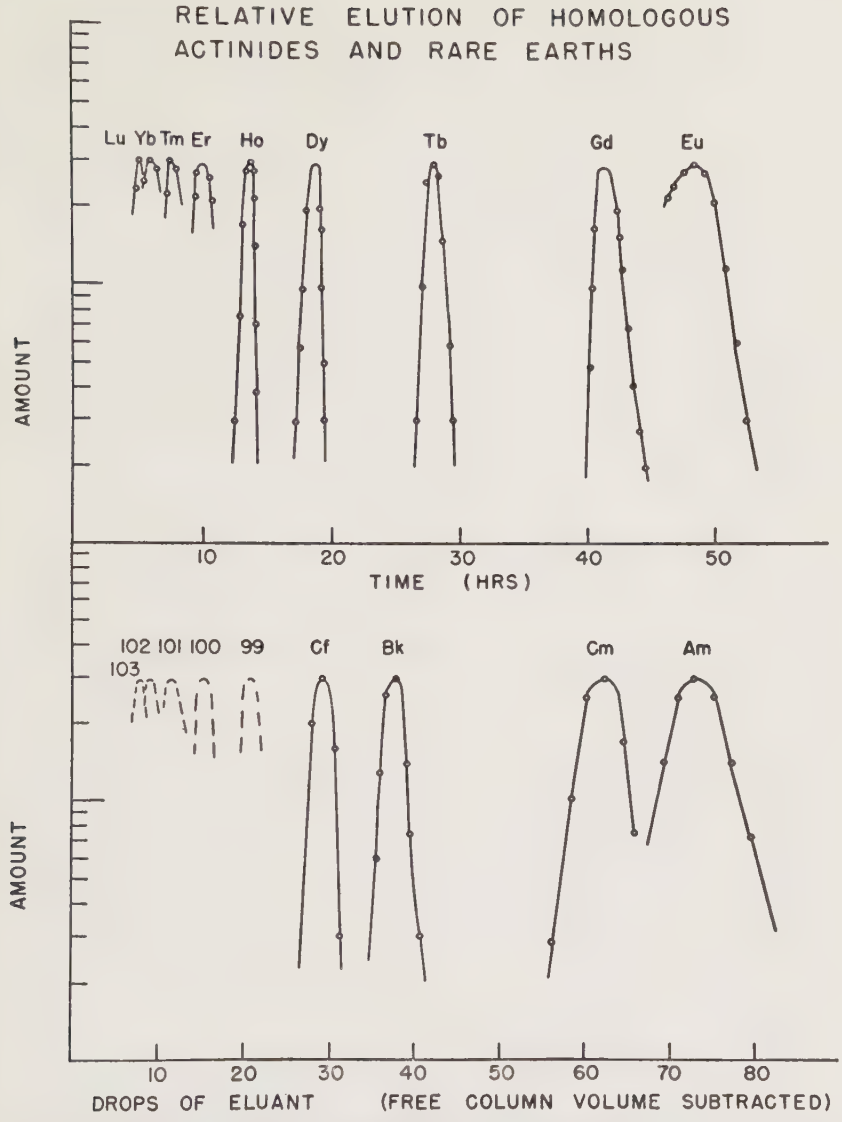


Fig. 2.12 Elution of homologous actinides (at 87°C) and lanthanides (at 100°C) from Dowex-50 resin with citrate.

material may then be placed at the top of a glass column filled with more of the organic polymer or resin which does not contain the actinides or lanthanides. The actinides or lanthanides can then be eluted from the resin by pouring through it the solution containing

the anion which forms complex ions with the actinide or lanthanide ions. In the well-behaved systems the lanthanide elements are eluted from the resin in the inverse order of their atomic numbers; that is, lutetium can be collected in the drops coming through the bottom of the column as the first element to emerge, ytterbium as the second element, and so on to cerium or lanthanum. The whole process bears a close resemblance to the well-known chromatography technique. Similarly for the actinides, the undiscovered element 103 will leave the column first, followed by element 102 and mendelevium (number 101) and so on down the scale of atomic numbers as shown in Fig. 2.12, which represents data taken in 1950 by S. G. Thompson, K. Street, Jr., and G. H. Higgins and shows the positions predicted for elements 103 and 102 and elements 101, 100, and 99 (all shown with broken lines) before any of these five elements were discovered. The cation-exchange resin Dowex-50 was used, and the elution was performed at 87°C with ammonium citrate buffered with citric acid to a pH of 3.5 (total citrate concentration 0.2 *M*). The same resin was used for the lanthanide elements in a somewhat longer column, and the elution, performed by B. H. Kettelle and G. E. Boyd, was performed at 100°C using a similar citrate buffer solution (pH 3.28). A remarkable analogy in the spacing can be seen between the californium-berkelium-curium-americium group and their rare-earth homologues, dysprosium-terbium-gadolinium-europium. The spacings reflect the relative changes in ionic radii which are a factor in determining the relative separations in the ion-exchange adsorption method.

The form in which the data are obtained will be further illustrated, using data from the actual discovery experiments, in the following sections.

2.8a Berkelium and Californium

The most important prerequisite to the process for making the transcurium elements was that sufficiently large amounts of americium and curium had to be manufactured to serve as target materials. Because of the intense radioactivity of these substances even in milligram or submilligram amounts, it was necessary to develop extremely efficient chemical separation methods in order to obtain the enormous separation factors needed for the isolation of the new

elements from the target material, so that it would be possible to detect the very small amounts of radioactivity due to them. This dangerous radioactivity of the source material made it necessary to develop complicated methods for remote control operation to keep the health hazards at a minimum.

With the aid of the Health Chemistry Group under the direction of N. B. Garden, these protection problems were solved; successful experiments were performed at the end of 1949 and the beginning of 1950. Americium for target material was prepared in milligram amounts by intense neutron bombardment of plutonium over a long period of time, and curium target materials were prepared in microgram amounts as the result of the intense neutron bombardment of some of this americium. Both of these neutron bombardments took place in high flux reactors. Element 97 was discovered by Thompson, A. Ghiorso, and the author in December 1949 as a result of the bombardment of the milligram amounts of Am^{241} with 35-Mev helium ions accelerated in the 60-inch cyclotron of the University of California at Berkeley. The first isotope produced has the mass number 243 and decays primarily by orbital electron capture, with a half life of 4.5 hours. Element 98 was first produced and identified similarly by Thompson, Ghiorso, Street, and the author in February 1950, at the University of California at Berkeley. The first isotope produced is now assigned the mass number 245 and decays by alpha-particle emission and orbital electron capture with a half life of 44 minutes. This isotope was produced by the bombardment of microgram amounts of Cm^{242} with 35-Mev helium ions accelerated in the 60-inch cyclotron. It is interesting to note that this identification of element 98 was accomplished with a total of only some 5,000 atoms; someone remarked at the time that this number was substantially smaller than the number of students attending the University.

The key to the discovery of these elements was chemical identification by the ion-exchange technique. The original data corresponding to these identifications are shown in Figs. 2.13 and 2.14 for elements 97 and 98, respectively. The cation exchange resin Dowex-50 was used and the elution was performed at 87°C with ammonium citrate buffered with citric acid to a pH of 3.5. In the case of element 97, preliminary separations from the target ameri-

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cium were made by a procedure which involved the oxidation of the americium to the VI state, the fluoride-soluble form, from which the element 97 was separated by coprecipitation with rare-earth fluoride. Preliminary separation of the element 98 from the target

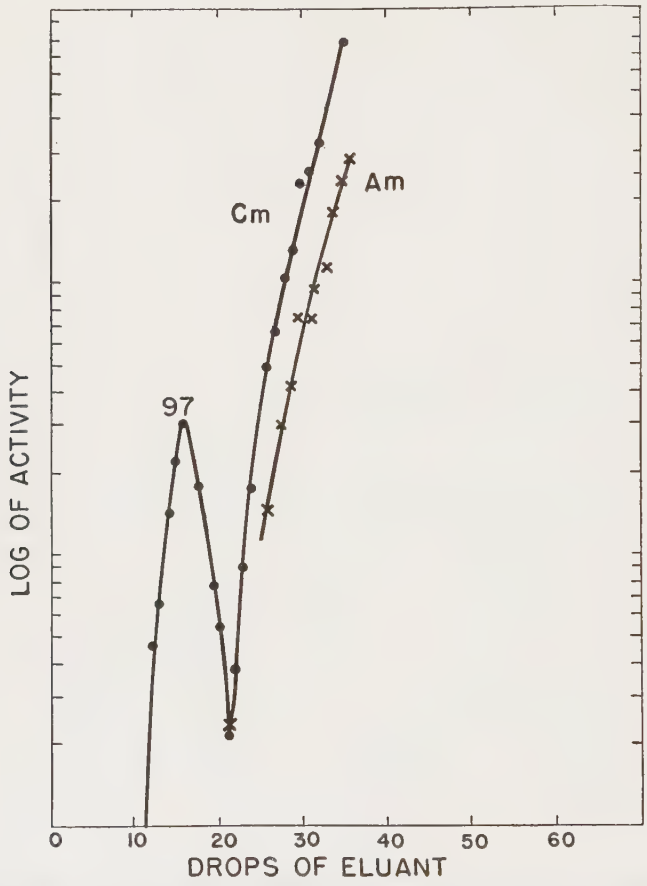


Fig. 2.13 Original elution data corresponding to discovery of berkelium (December 19, 1949). Activity due to Auger and conversion electrons (Bk) and alpha particles (Cm and Am). (Dowex-50 resin at 87°C with citrate elution.)

curium was effected by the ion exchange adsorption-elution procedure under the conditions just mentioned. It can be seen that these elements elute in the expected order ahead of curium. The final elution corresponding to the discovery of element 97 took

place on December 19, 1949, and that for element 98 took place on February 9, 1950.

The naming of elements 97 and 98 presents an interesting story.

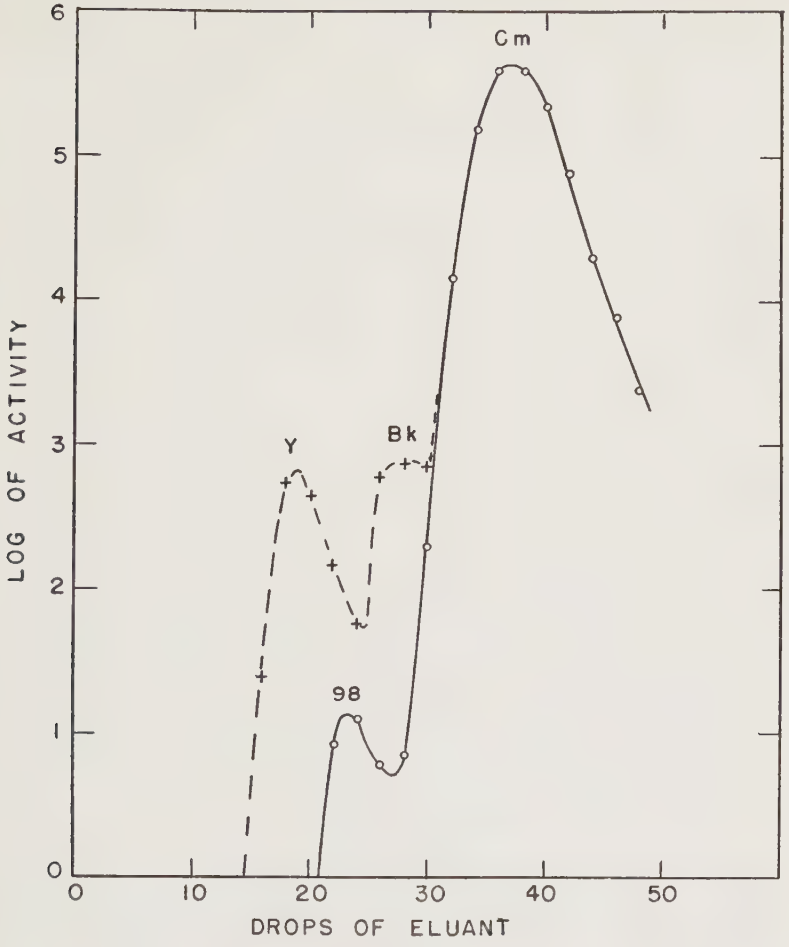


Fig. 2.14 Original elution data corresponding to the discovery of californium (February 9, 1950). Solid curve indicates alpha-particle counts/minute; dashed curve, Auger and conversion electrons and beta particles (and alpha particles). (Dowex-50 resin at 87°C with citrate elution).

Element 97 was called berkelium (symbol Bk) after the city of Berkeley, California, where it was discovered, as its rare-earth analogue, terbium (symbol Tb), was given a name derived from

Ytterby, Sweden, where so many of the early rare-earth minerals were found. Element 98 was named californium (symbol Cf) after the university and state where the work was done. This latter name, chosen for the reason given, does not reflect the observed chemical analogy of element 98 to dysprosium (symbol Dy), as "americium," "curium," and "berkelium" signify that these elements are the chemical analogues of europium, gadolinium, and terbium, respectively. In their announcement of the discovery of element 98 in the *Physical Review*, the authors made the comment, "The best we can do is point out in recognition of the fact that dysprosium is named on the basis of a Greek word meaning 'difficult to get at,' that the searchers for another element a century ago found it difficult to get to California."

Upon learning about the naming of these elements, the "Talk of the Town" section of the *New Yorker* magazine had the following to say:

New atoms are turning up with spectacular, if not downright alarming, frequency nowadays, and the University of California at Berkeley, whose scientists have discovered elements 97 and 98, has christened them berkelium and californium, respectively. While unarguably suited to their place of birth, these names strike us as indicating a surprising lack of public-relations foresight on the part of the university, located, as it is, in a state where publicity has flourished to a degree matched perhaps only by evangelism. California's busy scientists will undoubtedly come up with another atom or two one of these days, and the university might well have anticipated that. Now it has lost forever the chance of immortalizing itself in the atomic tables with some such sequence as universitium (97), ofium (98) californium (99) berkelium (100).

The discoverers sent the following reply:

"Talk of the Town" has missed the point in their comments on naming of the elements 97 and 98. We may have shown lack of confidence but no lack of foresight in naming these elements "berkelium" and "californium." By using these names first, we have forestalled the appalling possibility that after naming 97 and 98 "universitium" and "ofium," some New Yorker might follow with the discovery of 99 and 100 and apply the names "newium" and "yorkium."

The answer from the *New Yorker* staff was brief: "We are already at work in our office laboratories on 'newium' and 'yorkium.' So far we just have the names."

However, elements 99 and 100 were not destined to be named "newium" and "yorkium," as the account below will show.

Later work has, of course, led to much better elution curves. As an example we have Fig. 2.12 representing data obtained in 1950, as mentioned above. This figure makes it possible to compare the predicted elution positions (shown with broken lines) with the actual positions found upon the discovery of elements 99 and 100, to be described in the next section.

2.8b Einsteinium and Fermium

The story of the discovery of elements 99 and 100 represents an outstanding example of the unexpected in science. The seventh and eighth transuranium elements were discovered in debris from the "Mike" thermonuclear explosion which took place in the Pacific in November 1952. Debris from the explosion was collected first on filter papers attached to drone airplanes which flew through the clouds and, later, in more substantial quantity, gathered up as fallout materials from the surface of a neighboring atoll. This debris was brought to the United States for chemical investigation in a number of laboratories.

Initial investigation at the Argonne National Laboratory in Chicago and at the Los Alamos Scientific Laboratory of the University of California in New Mexico led to the unexpected observation of heavy isotopes such as Pu^{244} and Pu^{246}. At that time, the heaviest known isotope of plutonium was Pu^{243}. Since this pointed to the capture of many successive neutrons by the U^{238} in the device and thus the presence of neutron-excess isotopes in greater abundance than expected, a group at the University of California Radiation Laboratory undertook to look for isotopes of transcalifornium elements in this material. Ion exchange experiments of the type previously mentioned immediately demonstrated the existence of a new element. Later, in order to secure a larger amount of source material, it was necessary to work up many hundreds of pounds of coral from one of the atolls adjoining the explosion area. Eventually such coral was worked up by the ton, using bismuth phosphate as the carrier for the tripositive actinide elements, in a pilot-plant operation which went under the name of "Paydirt."

Without going into the details, it may be pointed out that the

experiments involving the groups at the three laboratories led to the positive identification of isotopes of elements 99 and 100. A twenty-day activity emitting alpha particles of 6.6-Mev energy was

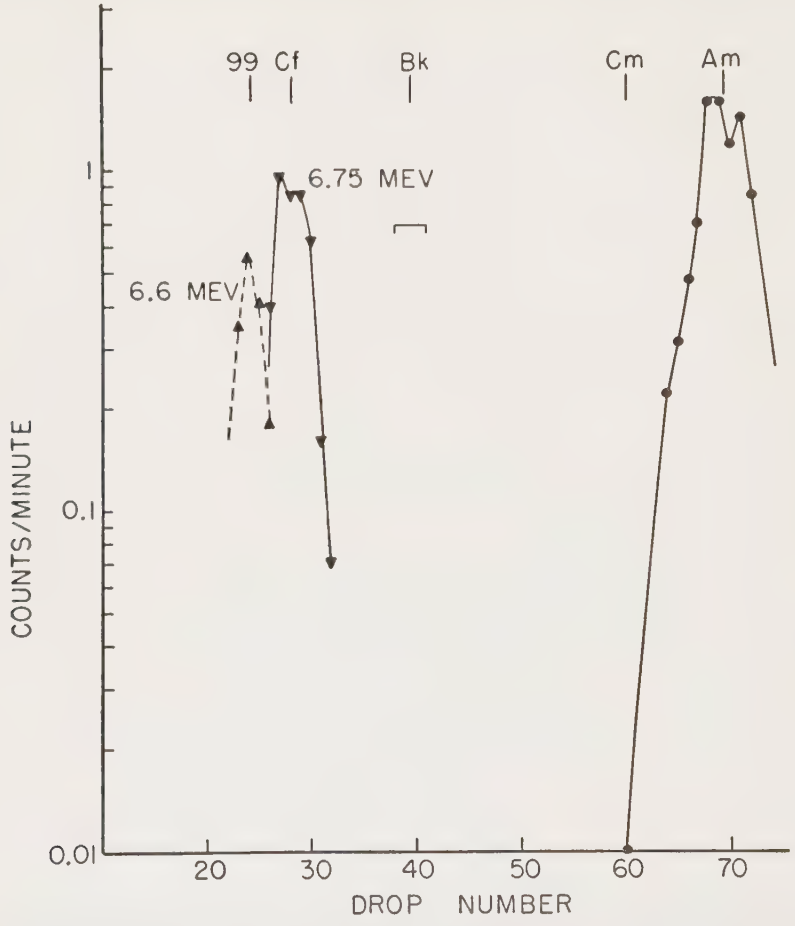


Fig. 2.15 Original elution data corresponding to discovery of einsteinium (December 19–20, 1952). Activity due to alpha particles. (Dowex-50 resin at 87°C with citrate elution.)

identified as an isotope of element 99 (with the mass number 253), and a 7.1-Mev alpha activity of 16 hours' half life was identified as an isotope of element 100 (with the mass number 255). The suc-

cessive instantaneous capture of many neutrons by U^{238} led to heavy uranium isotopes, as described in more detail in the following chapter. The heavy uranium isotopes decayed into the isotopes above them by the emission of negative beta particles. The original

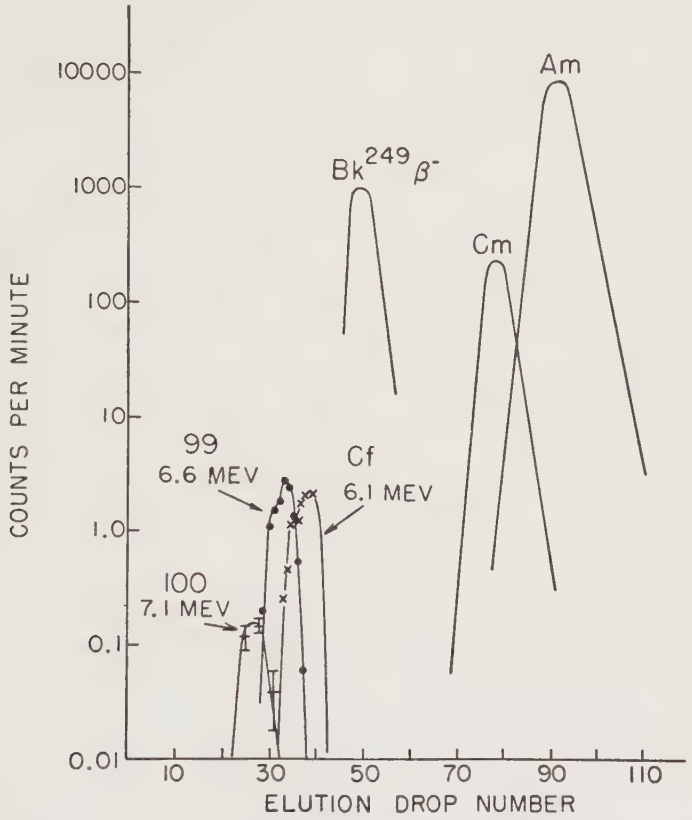


Fig. 2.16 Elution data for fermium corresponding to second chemical identification (March 1, 1953). Activity due to alpha particles. (Dowex-50 resin at 87°C with citrate elution.)

data for element 99, as recorded at Berkeley during the night of December 19–20, 1952, when this element was discovered, are plotted in the usual way in Fig. 2.15, from which it can be seen by comparison with Fig. 2.12 that the elution comes very approximately in the predicted eka-holmium position. Again the resin was

Dowex-50 and the elution was performed at 87°C with citrate ion at a pH of 3.5. Similarly, the elution data recorded on March 1, 1953, for element 100 are plotted in Fig. 2.16, from which it can be seen by comparison with Fig. 2.12 that its elution corresponds to the eka-erbium position. This followed the initial-discovery elution experiment, which took place at Berkeley on January 16, 1953, with such a small amount of element 100 that it is not possible to make the usual plot of a complete elution curve; this first identification of element 100 was made with about 200 atoms only. The most striking previous accomplishment in this category was the positive identification of element 98 with a total of about 5,000 atoms.

The large group of investigators included A. Ghiorso, S. G. Thompson, G. H. Higgins, and myself of the Radiation Laboratory and Department of Chemistry of the University of California; M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, and W. M. Manning of the Argonne National Laboratory; and C. I. Browne, H. L. Smith, and W. R. Spence of the Los Alamos Scientific Laboratory. These researchers suggested for element 99 the name einsteinium (symbol E) in honor of the great physicist, Albert Einstein, and for element 100, the name fermium (symbol Fm) in honor of the father of the atomic age, Enrico Fermi.

Before declassification and the subsequent announcement of the original discovery experiments could be accomplished, isotopes of elements 99 and 100 were produced by a number of other methods. Chief among these was that of successive neutron capture as the result of intense neutron irradiation in the high-flux Materials Testing Reactor (MTR) at the National Reactor Testing Station at Arco, Idaho (described below, Chapter 3). The difference between this method of production and that of the "Mike" thermonuclear explosion is one of time as well as of starting material. In a reactor it is necessary to bombard gram quantities of plutonium for two or three years; thus the short-lived intermediate isotopes of the various elements have an opportunity to decay. In the fission-fusion device larger amounts of uranium were subjected to an extremely high neutron flux for a period of microseconds; the subsequent beta decay of the ultraheavy isotopes of uranium led to the nuclides found in the debris.

Although it has been possible in this chapter to give only a brief review of the chemical properties of the actinide elements, it is to be hoped that some feeling for the interesting nature of this transition group from the chemist's point of view has been communicated. It is clear that the actinide character of the group and the analogy of its chemical properties with those of the lanthanide transition group has been the key to the discovery of many of the actinide elements.

Chapter 3. Nuclear Properties of the Transuranium Elements

This chapter will be devoted to a summary of the nuclear properties of the transuranium elements. As in the case of the chemical properties summarized in the previous chapter, the extent of the information is so large that it will be necessary to limit the selection to certain representative material. The nuclear reactions involved in the production of the nuclides in this region, reactions which include both neutron and charged-particle irradiations of target nuclei, will be discussed first. This will be followed by a consideration of the nuclear thermodynamics, or the masses of these heaviest nuclides. Next, the radioactive properties and nuclear energy states and their regularities will be discussed in terms of an applicable nuclear model. Finally, the important induced and spontaneous fission properties of these nuclides will be reviewed.

3.1 Nuclear Reactions

3.1a Neutrons

Most of the beta-stable nuclides and the nuclides which are unstable toward the emission of negative beta particles can be built up through the absorption of successive neutrons in some available starting material such as Pu^{239}. The sequences of neutron-capture reactions and beta decays, leading to nuclides as heavy as Fm^{254}, are shown in Fig. 3.1. When the irradiated material is present in the active core of a high-neutron-flux reactor, where fluxes of slow neutrons in excess of 10^{14} neutrons/cm^2/sec may be obtained, it is possible in the course of several years to build up appreciable yields

of nuclides which correspond to the absorption of some fifteen or more neutrons. An example of such a reactor is the Materials Testing Reactor (MTR) at the National Reactor Testing Station at Arco, Idaho, which has been the source of milligram-to-gram quantities of americium isotopes and of the lighter curium isotopes. The heavier curium isotopes, the berkelium isotope with mass number 249, and the beta-stable californium isotopes are available in weighable amounts from such a source, and this should soon be true for the einsteinium isotope with mass number 254. Neutron irradiation is also the best source for the production of the shorter-lived ein-

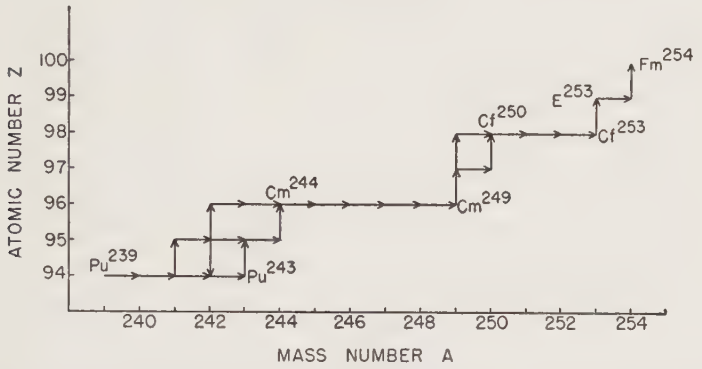


Fig. 3.1 Nuclear reaction sequences for production of heavy nuclides by intense slow neutron irradiation of Pu^{239}. The neutron-capture reactions are interspersed with beta decays.

steinium and fermium isotopes shown in the sequence in Fig. 3.1. The rate of build-up depends, of course, on the "slow neutron" or "pile neutron" cross sections for the various neutron-capture and fission reactions. Ideally the values for such cross sections should be known at specified neutron energies, and some of the nuclides which have been subject to careful investigation have cross-section values known for "thermal" energies or in some cases more specifically, for neutrons with an energy corresponding to a velocity of 2,200 meters per second or about 0.025 electron volts. Very often the measured cross-section values correspond to neutrons with an unspecified distribution of energy in the thermal region, dependent on the particular reactor conditions used in the measurements, and such neutrons may be loosely referred to as "slow" neutrons. Slow

TABLE 3.1 *Slow Neutron Fission and Capture Cross Sections*

ISOTOPE	FISSION σ_f (BARNS)	CAPTURE σ_c (BARNS)
Ra^{223}	<100	125 ± 15*
Ra^{224}		12.0 ± 0.5
Ra^{226}	$<1.1 \times 10^{-4}$	13.5 ± 1.5*
Ra^{228}	<2	36 ± 5
Ac^{227}	<2	516 ± 50*
Th^{227}	1500 ± 1000*	
Th^{228}	≤ 0.3	123 ± 15
Th^{229}	45 ± 11*	
Th^{230}	<0.001	26 ± 2
Th^{232}	<0.0002	7.55 ± 0.025*
Th^{233}	15 ± 2*	1400 ± 200
Th^{234}	<0.01	1.8 ± 0.5
Pa^{230}	1500 ± 250*	
Pa^{231}	0.010 ± 0.005*	200 ± 15*
Pa^{232}	700 ± 100	760 ± 100
Pa^{233}	<0.1	140 ± 20*
Pa^{234} (1.18 m)	<500	
Pa^{234} (6.7 h)	<5000	
U^{230}	25 ± 10*	
U^{231}	400 ± 300*	
U^{232}	80 ± 15*	300 ± 200
U^{233}	532 ± 6*	56 ± 2*
U^{234}	≤ 0.65	92 ± 7*
U^{235}	582 ± 10*	112 ± 10*
U^{236}		9 ± 2*
U^{238}	<0.5	2.76 ± 0.09*
U^{239}	15 ± 3*	22*
Np^{234}	900 ± 300*	
Np^{236}	2800 ± 800*	
Np^{237}	0.019 ± 0.003*	170 ± 22*
Np^{238}	1600 ± 100*	
Np^{239}	<3	35 ± 10 (to Np^{240m}) 25 ± 15 (to Np^{240})
Pu^{236}	210*	
Pu^{238}	18.4 ± 0.9*	403 ± 8*
Pu^{239}	738 ± 9*	287 ± 13*
Pu^{240}	<0.1	530 ± 50
Pu^{241}	950 ± 50*	390 ± 80
Pu^{242}	<0.3	18.6 ± 0.8*
Pu^{243}		170 ± 90
Pu^{244}		2.1 ± 0.3

TABLE 3.1 *Slow Neutron Fission and Capture Cross Sections (Continued)*

ISOTOPE	FISSION σ_f (BARNS)	CAPTURE σ_c (BARNS)
Pu^{245}		260 ± 145
Am^{241}	3.13 ± 0.15*	600*
Am^{242m}	3000*	3000
Am^{242}	6400 ± 500*	1600
Am^{243}	<0.072	73.6 ± 1.8*
Cm^{242}	<5	20 ± 10
Cm^{243}	690 ± 50*	250 ± 150
Cm^{244}		25 ± 10
Cm^{245}	1940 ± 300*	200 ± 100
Cm^{246}		15 ± 10
Cm^{247}	~ 200	~ 200
Cm^{248}		~ 2
Bk^{249}		~ 400
Cf^{249}	~ 630	$\sim 270 \pm 100$
Cf^{250}		~ 1500
Cf^{251}		~ 3000
Cf^{252}		~ 30
Cf^{253}		~ 40
Cf^{254}		<2
E^{253}		~ 200 (to E^{254m})
		~ 7 (to E^{254})
E^{254}	~ 2000	~ 40
E^{254m}		<10
E^{255}		~ 40

* Thermal neutrons.

or thermal neutron cross sections for both fission and capture are summarized, insofar as they are known, in Table 3.1, and the rates of build-up of some of the earlier isotopes in the sequence, for some specified conditions, are shown in Fig. 3.2. The rate of build-up of such isotopes depends on the fission cross sections as well as on the neutron-capture cross sections of the isotopes involved. Thus nonfissionable Pu^{242} is a much better starting material than Pu^{239}, not only because it is heavier, but because so much less material is lost through the fission process.

An important aspect of the slow-neutron capture reactions is the "resonances" which are generally found. The sharp resonance peaks found in the plot of cross section versus neutron energy are

due to the capture of neutrons with kinetic energies such that the binding plus kinetic energy is very close to the energy of some level in the excited nucleus. Examples of this are shown in Fig. 3.3, which plots the data for the *total* neutron cross sections for the non-slow-neutron-fissionable nuclides Th^{232} and U^{238} from the Brookhaven compilation of D. J. Hughes and J. A. Harvey. Similar

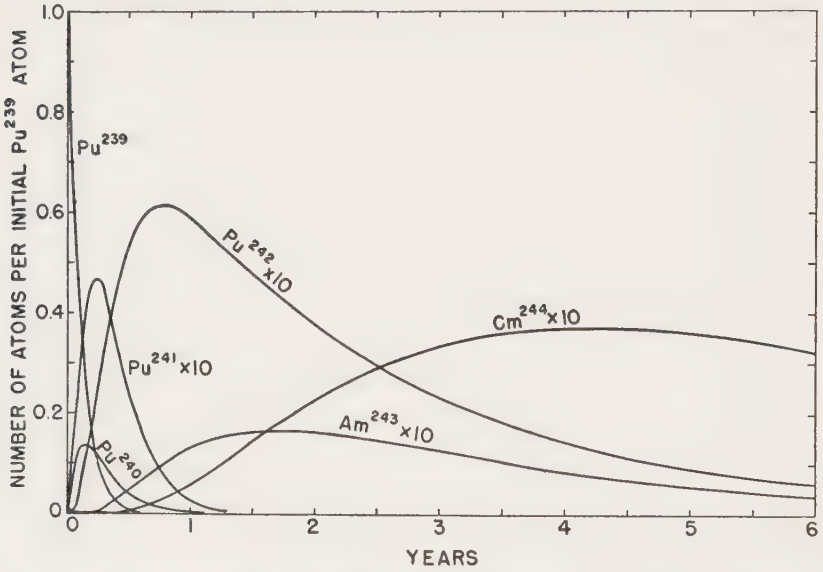


Fig. 3.2 Production of some heavy nuclides by irradiation of Pu^{239} at a flux of 3×10^{14} neutrons per sq. cm. per second. The relevant neutron-capture and fission cross sections are to be found in Table 3.1.

resonance peaks are found in nuclei which are fissionable with slow neutrons, generally at the same energies as the resonances for the fission process. Examples of such curves showing resonances for fission, for the nuclides U^{233}, U^{235}, and Pu^{239} are shown later in Fig. 3.25.

Another method of synthesis was referred to in Chapter 2 in connection with the discovery of the elements with atomic numbers 99 and 100. This method became evident in the analysis of debris from the "Mike" shot of the 1952 series of weapons tests carried out at the Pacific Proving Grounds of the United States Atomic Energy Commission. In this test explosion, which was in the mega-

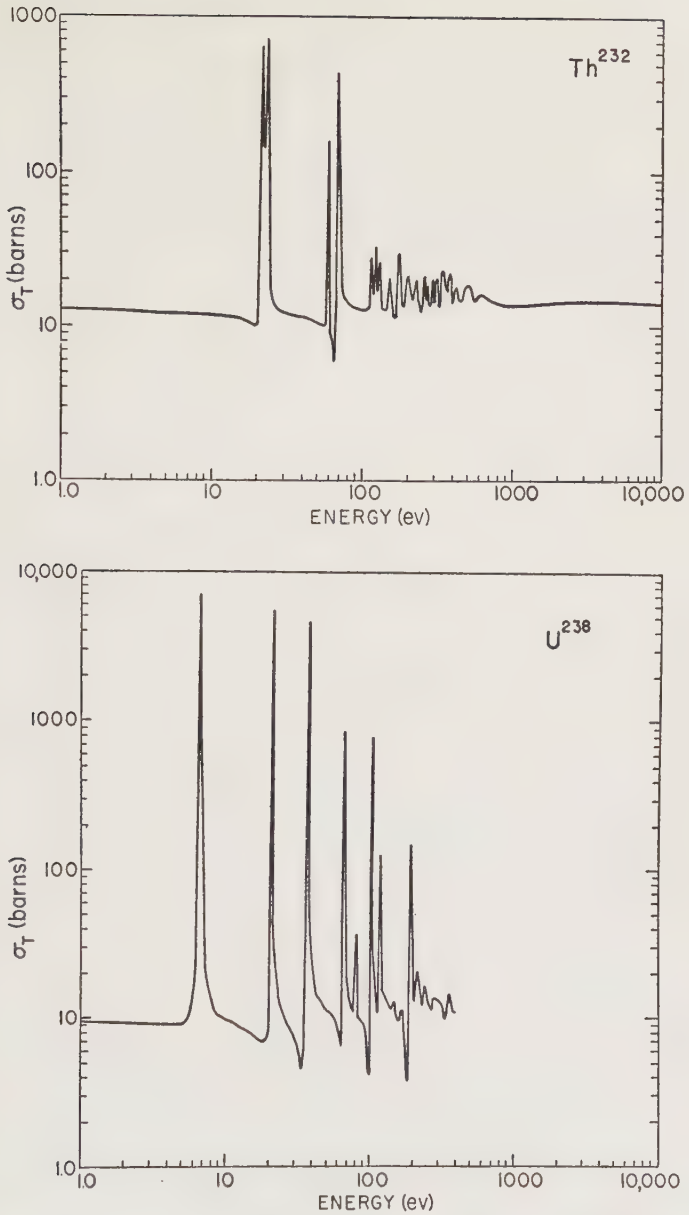


Fig. 3.3 Variation of total neutron cross section with energy for Th^{232} and U^{238}.

ton class, an instantaneous neutron flux many orders of magnitude greater than that available in the MTR reactor was available for a fraction of a second. By nuclear chemical studies of the material collected after this explosion, it was deduced that $_{99}E^{253}$ and $_{100}Fm^{255}$ had been produced from the U^{238} which was present in the explosive device. This represents the successive instantaneous capture of fifteen and seventeen neutrons by the uranium. This synthesis has

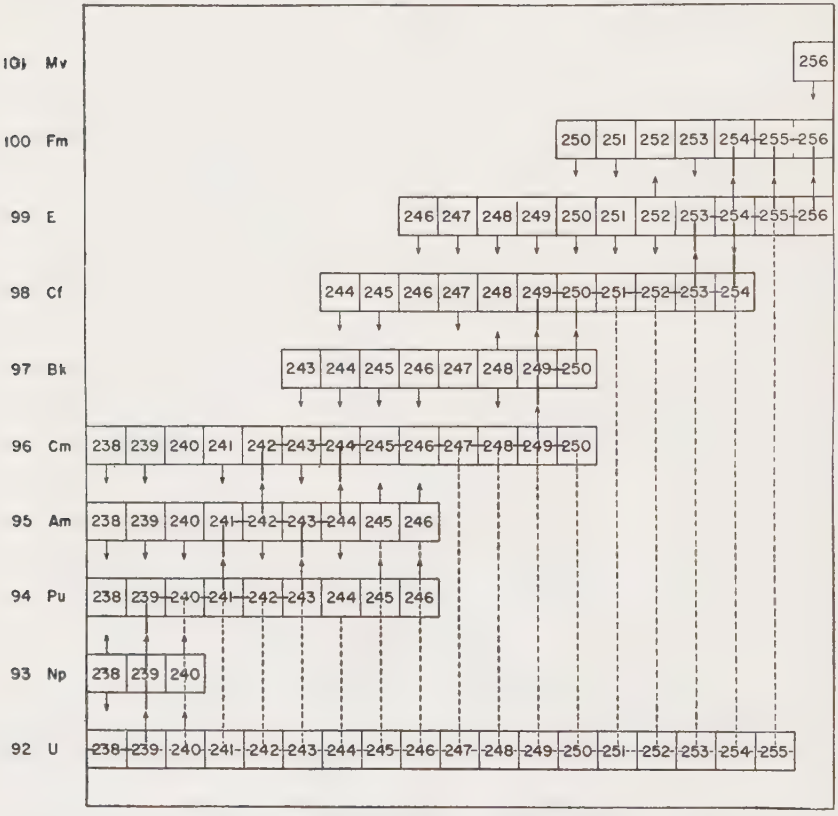


Fig. 3.4 Nuclear reactions for first production of einsteinium and fermium, as well as other nuclides, in the "Mike" thermonuclear explosion. The neutrons are added instantaneously to U^{238} to form U^{239} to U^{255} which undergo slow beta decay as shown by dotted lines. The solid lines show the build-up of nuclides by slow neutron irradiation of U^{238}, Pu^{239}, or heavier nuclides; in this case, the beta decays are interspersed with neutron-capture reactions with respect to time. The small arrows pointing up indicate that these isotopes decay by the emission of a negative beta particle. The arrows pointing down indicate that these isotopes decay by the capture of orbital electrons.

one important difference from the nuclear-reactor approach outlined in Fig. 3.1. Since the neutrons are captured within a fraction of a second, rather than over a period of months or years, there is no opportunity for beta decay to occur during the synthesis. Beta decay probably will, in general, not proceed with a half life shorter than about 0.1 sec. The production of $_{100}Fm^{255}$ in this explosion must be via the production of U^{255} from U^{238}, followed by a long chain of short-lived beta decays, $U^{255} \xrightarrow{\beta^-} Np^{255} \xrightarrow{\beta^-} Pu^{255}$, etc. ending with Fm^{255}, all of which occur after the neutron capture reactions are completed. These reactions are illustrated in Fig. 3.4, which also includes a summary of the alternative way of building up heavy nuclides through irradiation with slow neutrons as is also illustrated in Fig. 3.1.

3.1b Charged Particles

The reactions produced in the transuranium elements by charged particles such as protons, deuterons, and helium ions have some special features associated with them as a result of the strong competition with fission. (The reactions induced by heavier ions will be discussed in Chapter 4.) Most of the work on transmutations with these charged particles has been in the energy range below 50 Mev, where the compound-nucleus picture might be expected to be applicable. However, this concept has only limited applicability in accounting for the spallation reactions which survive the fission process. The spallation (i.e. nonfission reactions) cross sections are all small, and the fission cross sections are large. The proportion of fission is already greater than 90 per cent at plutonium and increases with increasing atomic number of the target nucleus.

Consideration of a number of measured excitation functions for such reactions carried on largely in our Laboratory leads to the following conclusions. The observed small spallation and large fission cross sections indicate that fission competes successfully for most of the total reaction cross section in the energy range studied. The relatively high cross sections ("tails") evident in the spallation excitation functions beyond their maxima constitute evidence for processes other than compound-nucleus formation, e.g. direct interactions. Even more convincing evidence for non-compound-

nucleus processes is seen in the fact that the cross sections for (α,pxn) reactions are of the same order of magnitude as the cross sections for (α,xn) reactions. The explanation of the prominent (α,pxn) reactions and the high-energy extensions ("tails") on the excitation functions rests strongly on the supposition that the ejection of high-energy protons, deuterons, and tritons occurs, leading to residual intermediate nuclei of such low excitation energy that they then escape the fission reaction. In fact, the measured yield of tritium is, in general, nearly equal to the yield of the corresponding radioactive spallation product which is formed. The relatively high yield of (p,pxn), (d,dxn), and $(\alpha,\alpha xn)$ reactions may also indicate the direction ejection of neutrons.

This description of the escape of small-particle emission reactions from fission competition is believed to have wide application for the explanation of spallation cross-section data in the heaviest element region. This heavy region is well suited to the study of such reactions, because survival of the slightly excited intermediate nucleus formed when high energy particles are emitted in a direct interaction is more likely than survival of the more highly excited compound nucleus formed by the union of target and projectile, owing to the greater loss of the latter by competition from fission as the excitation energy is expended by neutron evaporation. Further work is required to determine the relative importance of stripping, knock-on, pick-up, and "local excitation" reactions or possible combinations of these. However, some of the information on spallation reactions, principally the excitation function peaks for the $(\alpha,2n)$, $(\alpha,3n)$, $(\alpha,4n)$, $(d,2n)$, $(d,3n)$, etc. reactions fits to some extent into a general picture of compound-nucleus formation followed by particle evaporation, and, significantly, it is the probabilities for these reactions that are greatly reduced by fission competition.

These considerations are best illustrated with the aid of some composite, or generalized, excitation functions for bombardments with charged particles in the transuranium or heaviest element region. Fig. 3.5 shows such a typical pattern of excitation functions for reactions induced by helium ions. The peak cross sections for the $(\alpha,2n)$, $(\alpha,3n)$, and $(\alpha,4n)$ decrease as one goes to elements with higher atomic number or to neutron-deficient isotopes of a

given element. The excitation functions for the (α,n), (α,p), and $(\alpha,H^3+\alpha,p2n)$ reactions vary little as one goes from one heavy element target to another. The $(\alpha,d+\alpha,pn)$ excitation functions have not been very well characterized in the heavy elements and have not been shown. Fig. 3.6 shows similarly such generalized excitation

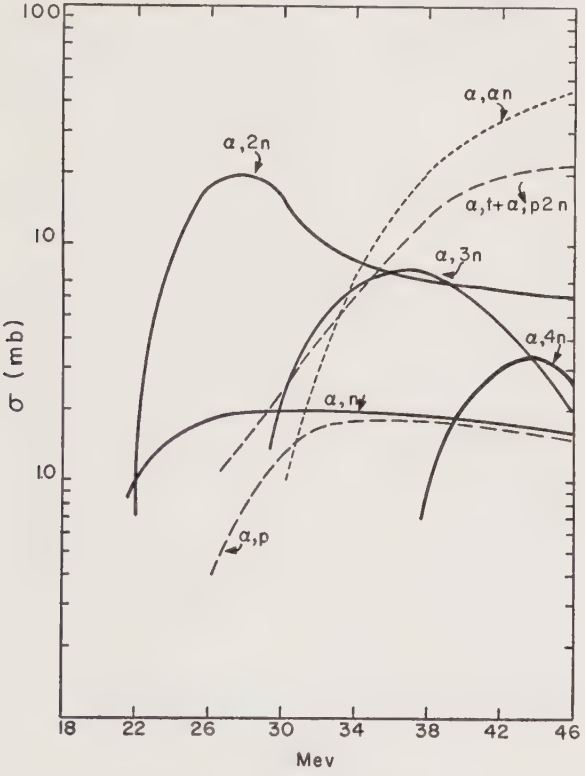


Fig. 3.5 Generalized excitation functions for helium ion-induced reactions in heavy elements. Based on data by R. J. Carr, A. Chetham-Strode, Jr., J. W. Cobble, P. F. Donovan, B. M. Foreman, Jr., A. Ghiorso, W. M. Gibson, R. A. Glass, J. Gonzalez-Vidal, B. G. Harvey, T. Sikkeland, T. D. Thomas, S. G. Thompson, W. H. Wade, R. Vandenbosch, the author, and co-workers.

functions for deuteron-induced reactions in these elements. The peak cross sections for the $(d,2n)$ and $(d,3n)$ vary with the characteristics of the target in the same way as for helium-ion-induced reactions. The (d,n) and (d,p) excitation functions are very similar for all heavy element targets which have been investigated; these

reactions presumably proceed by a stripping mechanism, often leaving the nucleus with so little excitation that it does not undergo fission.

Bombardments at higher energies (above 50 Mev) are not generally used to produce nuclides of transuranium elements, except

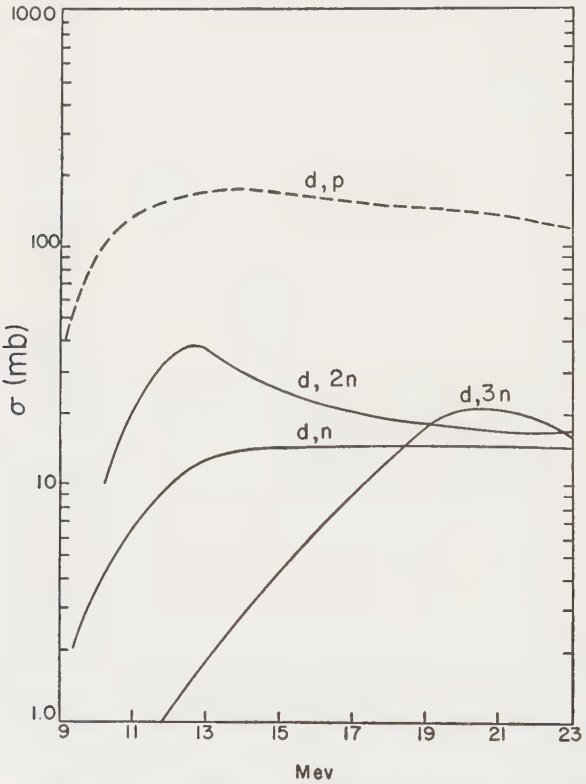


Fig. 3.6 Generalized excitation functions for deuteron-induced reactions in heavy elements. Based on data by A. Chetham-Strode, Jr., A. Ghiorso, W. M. Gibson, R. A. Glass, J. Gonzalez-Vidal, B. G. Harvey, S. G. Thompson, W. H. Wade, R. Vandenbosch, the author, and co-workers.

for some of the more neutron-deficient ones. A number of excitation functions for spallation reactions produced by protons, deuterons, helium ions on thorium, and protons on uranium have been determined for the energy region up to hundreds of Mev by W. W. Meinke, G. C. Wick, and the author and by M. Lindner and

R. N. Osborne. The results are in general agreement with the reaction model of R. Serber, in which the components of the incident projectile interact with individual nucleons of the target nucleus to initiate nuclear cascades, following which the cascade particles may either distribute their energy to other nucleons through collisions or may escape from the nucleus with little or no energy loss. This cascade mechanism will result in a rather wide distribution of residual excitation energy which can be dissipated by particle evaporation, or more probably by fission, leading to spallation cross sections as small as fractional millibarns for the production of quite neutron-deficient nuclides from uranium. Thus after the initiation of the spallation reaction by the direct interaction-cascade mechanism, the competition from fission affects the excitation function in a manner similar to that described above. In a still higher energy region, investigations with protons of energies up to billions of electron volts have been made. When the energy is sufficient to produce pions, these may be reabsorbed before they leave the nucleus and hence provide other mechanisms for energy utilization. M. L. Perlman and other investigators from the Brookhaven National Laboratory, the University of Chicago, and the Los Alamos Scientific Laboratory have proposed a "fragmentation" process, in which the kinetic energy and rest mass of the pion cause local heating, leading to dissociation of the nucleus into fragments of varying sizes in a time short compared to that required for equipartition of energy; the highly excited fragments will then evaporate nucleons with the result that the final products will have atomic numbers considerably removed from that of the target.

3.2 Nuclear Thermodynamics

The energy relationships among the isotopes in the transuranium region, i.e. the nuclear thermodynamics of this region, will be discussed next. These data are best summarized in the form of the atomic masses of these nuclides. The data presented in the following figures and tables represent a revision of the data of R. A. Glass, S. G. Thompson, and the author, using newer information now available.

In the heavy element region the existence of alpha- and beta-

decay instability in the same nucleus has made it possible to construct closed decay-energy cycles. Such cycles are extremely useful in checking the internal consistency of the decay data and in predicting unknown properties. Consider, for example, the cycles shown in Fig. 3.7 involving a few isotopes of the $4n + 1$ family. In the cycle containing Np^{237}, Am^{241}, Pu^{241}, and U^{237}, experimental data are available on all four sides of the data cycle, and these are mutually consistent—that is, the summation of decay energies around the complete cycle is essentially zero. In those cases where experimental data or reliable estimates are available for three

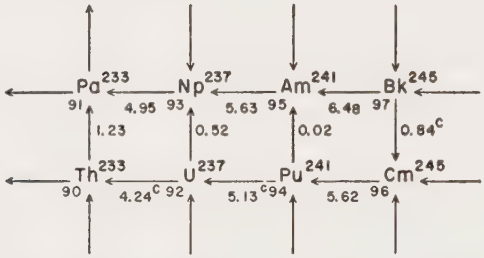


Fig. 3.7 Decay cycles for part of the $4n + 1$ family. Arrows ← mean α decay, ↑ β^- decay, ↓ electron capture decay. Numbers indicate total decay energies in Mev; those with superscript c are calculated by closing the cycles; those unmarked represent measured values.

branches of the cycle, the fourth can then be calculated by difference. A systematic extension of the closed decay energy cycle method to cover the entire transuranium element region is given in Figs. 3.8, 3.9, 3.10, and 3.11; the alpha disintegration energy includes in each case the recoil energy of the daughter nucleus.

Since alpha decay decreases the mass number of a decaying nucleus by four and beta processes leave the mass number unchanged, all isotopes in a given figure differ in mass number by multiples of four. Hence, four such figures are required to present the data for the $4n$, $4n + 1$, $4n + 2$, and $4n + 3$ mass types.

In Figs. 3.8 to 3.11 approximately one-fourth of the energy values listed represent directly determined values. Approximately one-half of the values were estimated from the graphs showing systematic trends in alpha and beta disintegration energies which will be discussed below. A final group of energies was calculated

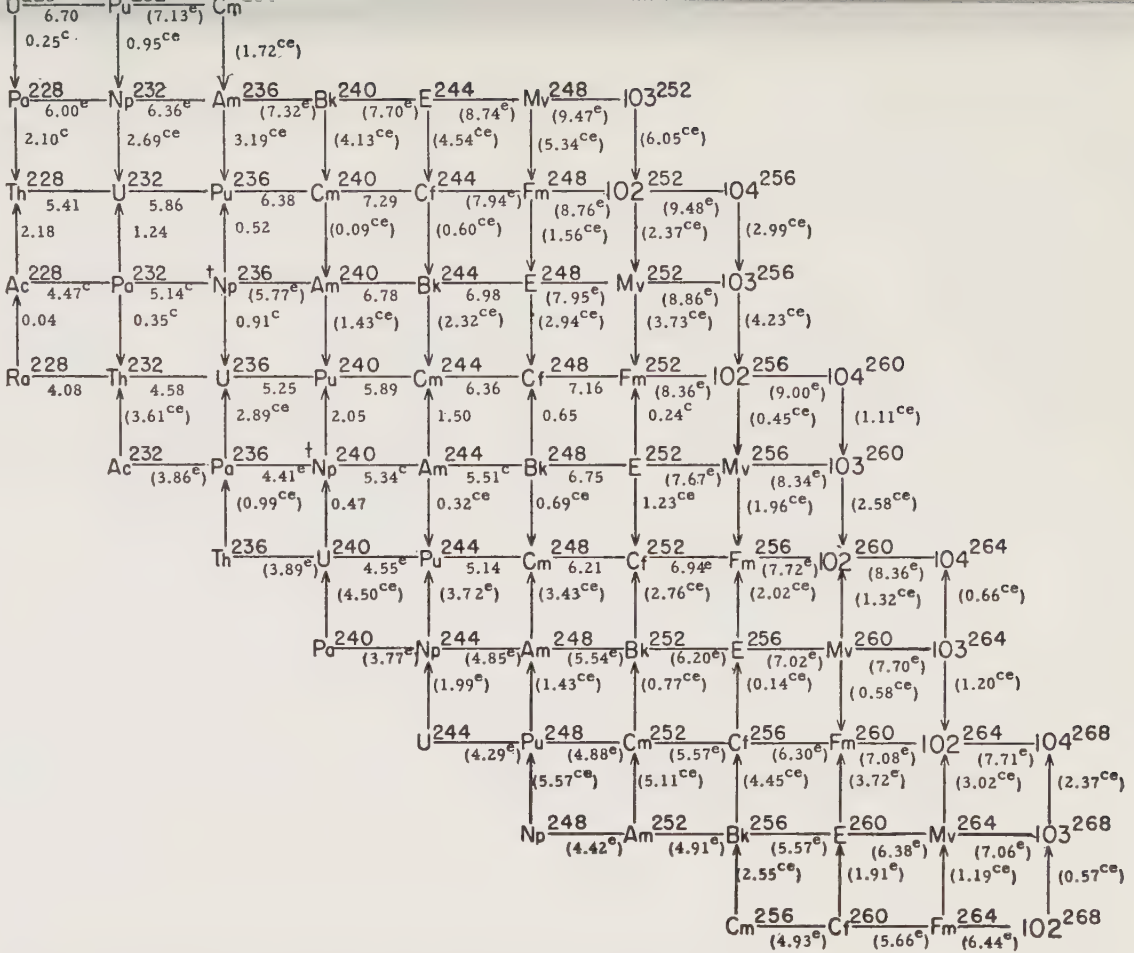


Fig. 3.8 Closed-decay energy cycles for the 4*n* family. No superscript indicates measured energy; *c*, energy calculated by closing cycle; *e*, energy estimated by methods given in text; *ce*, energy calculated from cycle containing estimated energy; †, denotes isomer; parentheses mean energy uncertain by more than 0.1 Mev.

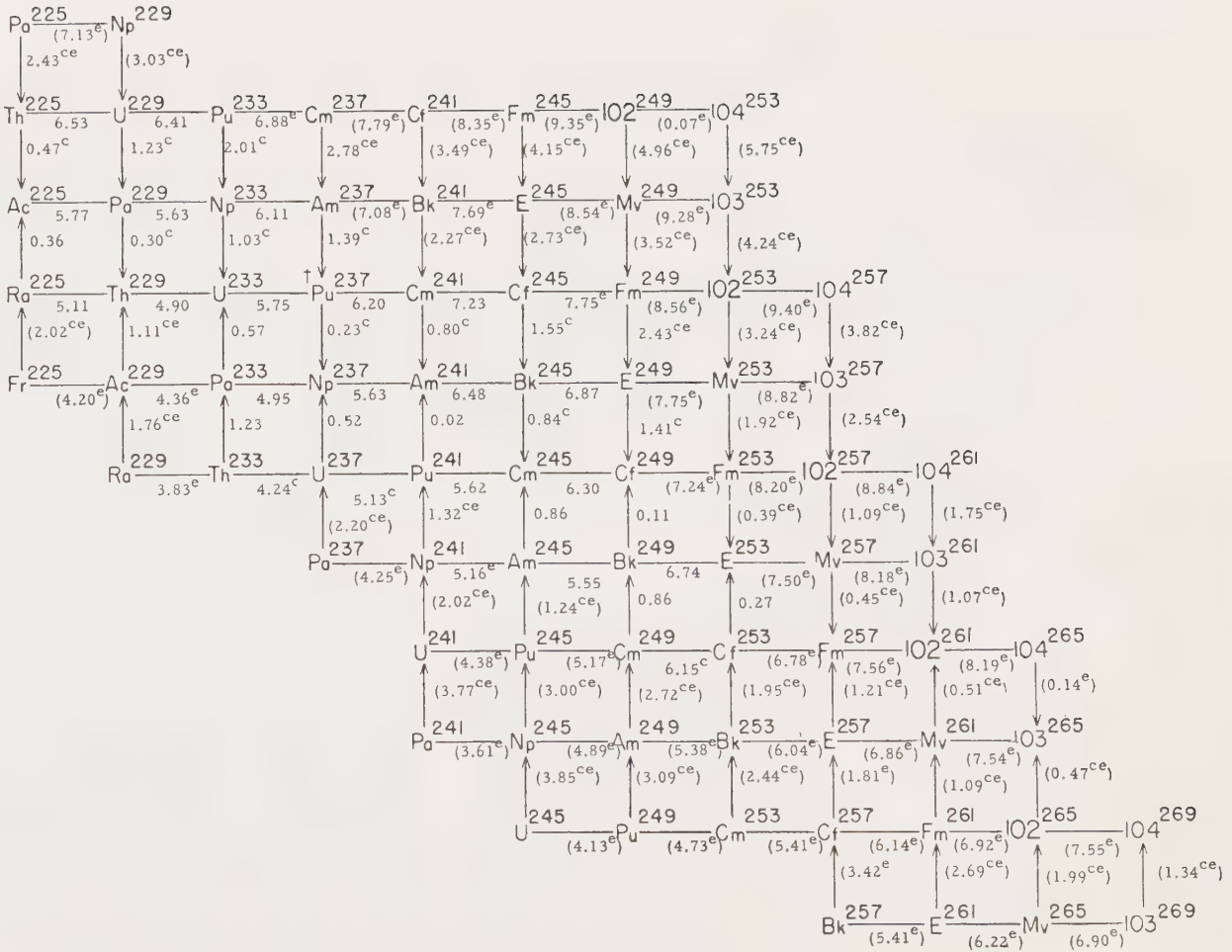


Fig. 3.9 Closed-decay cycles for the $4n + 1$ family. No superscript indicates measured energy; *c*, energy calculated by closing cycle; *e*, energy estimated by methods given in text; *ce*, energy calculated from cycle containing estimated energy; † denotes isomer; parentheses mean energy uncertain by more than 0.1 Mev.

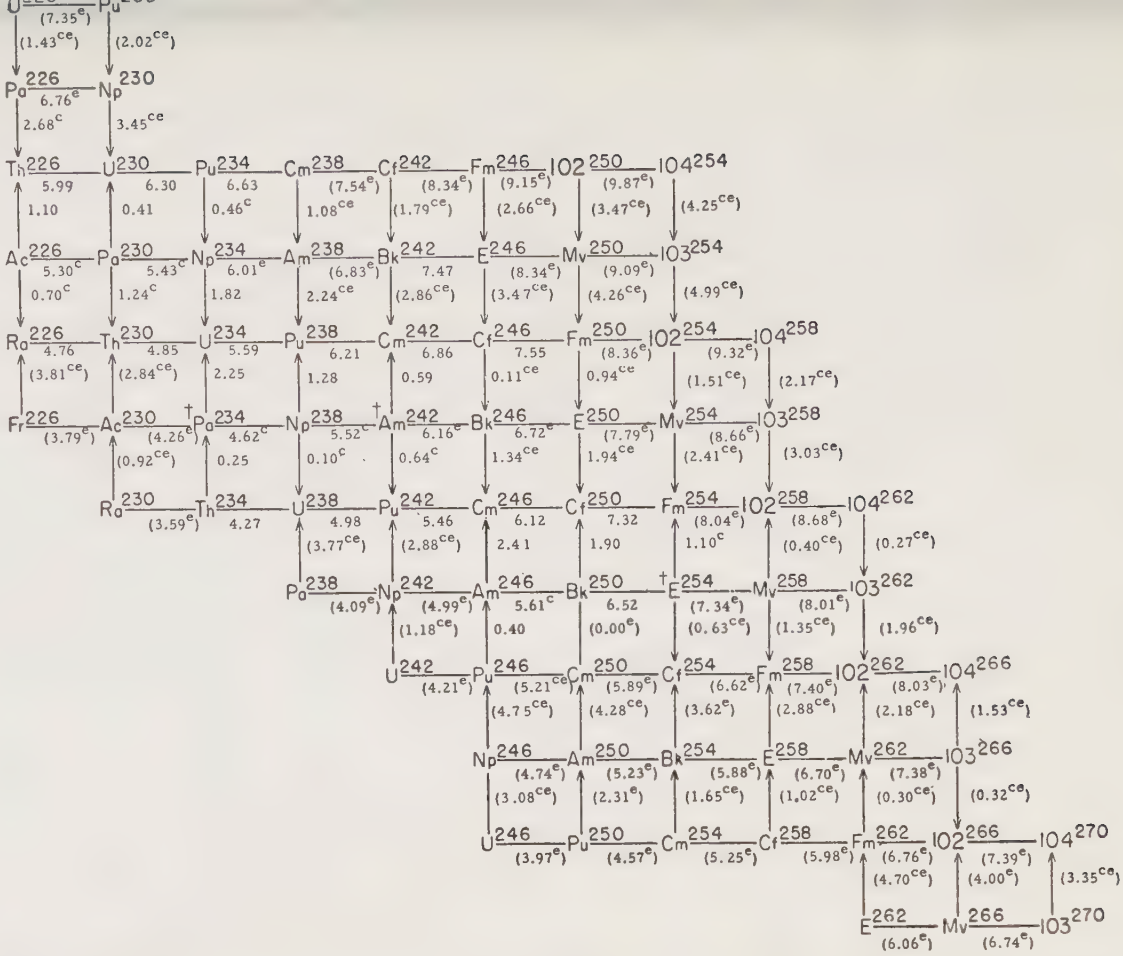


Fig. 3.10 Closed-decay energy cycles for the $4n + 2$ family. No superscript indicates measured energy; *c*, energy calculated by closing cycle; *e*, energy estimated by methods given in text; *ce*, energy calculated from cycle containing estimated energy; †, denotes isomer; parentheses mean energy uncertain by more than 0.1 Mev.

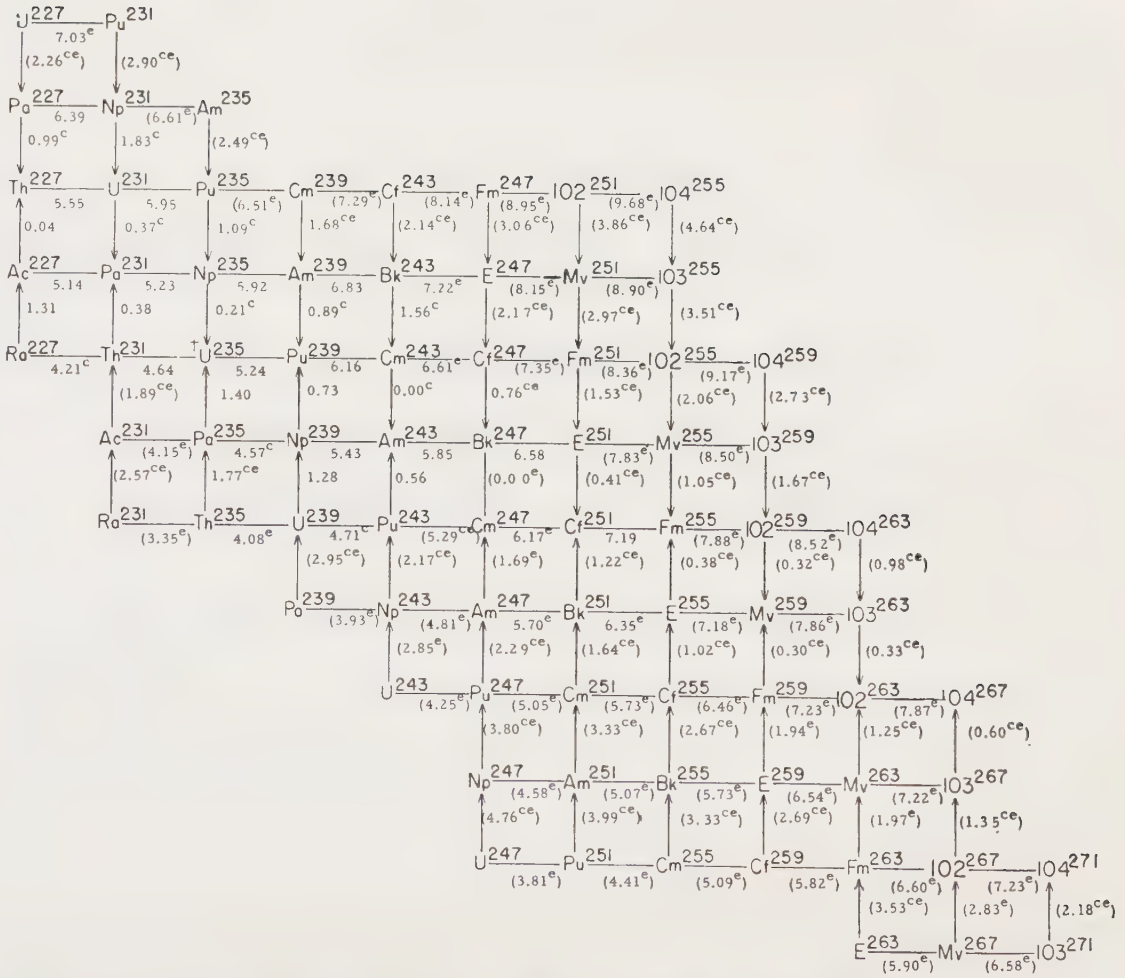


Fig. 3.11 Closed-decay energy cycles for the $4n + 3$ family. No superscript indicates measured energy; *c*, energy calculated by closing cycle; *e*, energy estimated by methods given in text; *ce*, energy calculated from cycle containing

by closing decay cycles after the experimental and estimated values were entered. Since any given disintegration energy is generally common to two decay cycles, opportunities arise for cross-checking the experimental or estimated values.

In the construction of Figs. 3.8 to 3.11 any inconsistencies which arose (usually in the vertical branches) were settled after due consideration of possible sources of error, and suitable adjustments were made to give the best possible self-consistent set of decay energies. These energy cycles refer only to the ground-state transitions and provide no information on decay to excited levels in the daughter nucleus. In general, decay energies associated with the ground state isomer are used in these cycles; nuclides with higher lying isomers are denoted by the symbol †.

The energy data for the four mass types presented in Figs. 3.8 to 3.11 can be interrelated and used to calculate the exact masses of all the transuranium isotopes, provided that at least one mass is determined on an absolute scale and that certain neutron-binding energies are known. Since the most reliable and complete experimental data on absolute masses and on neutron-binding energies are available in the region of lead, it is necessary to extend the closed-decay cycle plots to include isotopes in this region.

This has been done by R. A. Glass, S. G. Thompson, and the author, who also selected the following "best values" for neutron-binding energies to interrelate the four mass types: $Pb^{206-207}$, 6.73 Mev; $Pb^{207-208}$, 7.38 Mev; and $Pb^{208-209}$, 3.87 Mev. These values were chosen after considering data from certain nuclear reactions, namely: (a) energy thresholds for reactions such as $Pb^{207}(\gamma,n)Pb^{206}$; (b) determination of the capture gamma-ray spectra in a reaction of the type $Pb^{207}(n,\gamma)Pb^{208}$; and (c) measurement of the deuteron and proton energies in a reaction like $Pb^{208}(d,p)Pb^{209}$.

The absolute masses of the nuclides have then been calculated from their energies relative to the absolute mass of Pb^{208}. The value adopted for this compilation is 208.04140 (physical scale). In Table 3.2 this number of significant figures is carried throughout the calculations to be consistent with the *relative* accuracy of many of the energy values. Additional quantities which enter into these mass calculations are the mass of the helium atom, 4.00387, mass

TABLE 3.2 *Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements*

ELEMENT	MASS	B_n	B_p
92-Uranium	(226.09978)		(4.49)
	(227.10201)	(6.29)	(4.07)
	228.10236	(8.04)	5.00
	229.10473	6.15	5.12
	230.10567	7.49	5.48
	231.10836	5.87	5.49
	232.10952	7.28	6.13
	233.11223	5.84	6.30
	234.11386	6.84	6.63
	235.11722	5.24	6.70
	236.11927	6.46	7.08
	237.12259	5.27	7.38
	238.12501	6.11	(7.53)
	239.12888	4.76	(7.74)
	240.13149	5.94	(8.11)
	(241.13556)	(4.57)	(8.29)
	(242.13859)	(5.54)	(8.53)
	(243.14321)	(4.07)	
	(244.14638)	(5.41)	
	(245.15149)	(3.60)	
	(246.15539)	(4.73)	
	(247.16084)	(3.30)	
93-Neptunium	(229.10799)		(2.34)
	230.10938	(7.07)	3.26
	231.11032	7.49	3.25
	232.11241	6.42	3.81
	233.11333	7.50	4.03
	234.11582	6.05	4.24
	235.11745	6.85	4.24
	236.12024	5.76	4.77
	237.12203	6.70	5.01
	238.12511	5.49	5.23
	239.12751	6.14	5.25
	240.13098	5.13	5.63
	241.13339	6.12	5.81
	(242.13732)	(4.70)	(5.94)
	(243.14014)	(5.74)	(6.13)
	(244.14424)	(4.55)	(6.62)
	(245.14736)	(5.46)	(6.67)
	(246.15208)	(3.96)	(7.03)
	(247.15572)	(4.98)	(7.27)
	(248.16084)	(3.60)	(7.58)

TABLE 3.2 *Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements (Continued)*

ELEMENT	MASS	B_n	B_p
94-Plutonium	(230.11155)		(4.27)
	(231.11344)	(6.61)	(3.80)
	232.11343	(8.37)	4.69
	233.11549	6.44	4.71
	234.11631	7.60	4.81
	235.11862	6.22	4.97
	236.11969	7.37	5.50
	237.12228	5.95	5.69
	238.12374	7.00	5.99
	239.12672	5.59	6.08
	240.12878	6.45	6.40
	241.13197	5.39	6.66
	242.13423	6.26	6.80
	243.13781	5.03	(7.12)
	244.14024	6.10	(7.49)
	(245.14413)	(4.74)	(7.68)
	246.14698	(5.71)	(7.93)
	(247.15164)	(4.03)	(7.99)
	(248.15486)	(5.37)	(8.39)
	(249.15980)	(3.76)	(8.55)
	(250.16353)	(4.89)	
	(251.16880)	(3.46)	
95-Americium	(235.12129)		(2.94)
	236.12311	(6.67)	3.40
	237.12377	7.75	3.78
	238.12615	6.15	3.98
	239.12768	6.94	3.91
	(240.13031)	(5.91)	(4.24)
	241.13195	(6.84)	4.63
	242.13492	5.60	4.84
	243.13721	6.23	4.80
	244.14059	5.22	5.00
	245.14280	6.30	5.20
	246.14655	4.87	(5.33)
	(247.14918)	(5.92)	(5.53)
	(248.15332)	(4.51)	(6.02)
	(249.15648)	(5.42)	(6.07)
	(250.16105)	(4.11)	(6.42)
	(251.16452)	(5.14)	(6.66)
	(252.16946)	(3.76)	(6.97)

TABLE 3.2 *Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements (Continued)*

ELEMENT	MASS	B_n	B_p
96-Curium	(236.12496)		(4.17)
	237.12675	(6.69)	4.19
	238.12731	7.85	4.29
	239.12948	6.34	4.47
	240.13041	7.50	5.04
	241.13281	6.13	(5.26)
	242.13428	6.99	5.41
	243.13721	5.64	5.44
	244.13898	6.72	5.94
	245.14188	5.66	6.38
	246.14397	6.42	6.50
	(247.14737)	(5.20)	(6.82)
	248.14964	(6.25)	(7.16)
	249.15356	4.71	(7.36)
	(250.15645)	(5.67)	(7.61)
	(251.16094)	(4.19)	(7.68)
	(252.16397)	(5.54)	(8.09)
	(253.16875)	(3.91)	(8.24)
	(254.17231)	(5.05)	
	(255.17741)	(3.62)	
	(256.18134)	(4.70)	
97-Berkelium	(240.13485)		(2.59)
	(241.13525)	(7.99)	(3.08)
	(242.13735)	(6.40)	(3.35)
	243.13889	(6.94)	3.29
	(244.14147)	(5.96)	(3.62)
	245.14278	(7.14)	4.04
	246.14540	5.92	4.30
	247.14737	6.54	4.41
	248.15038	5.56	(4.78)
	249.15264	6.26	4.79
	250.15645	4.81	4.89
	(251.15918)	(5.83)	(5.04)
	(252.16314)	(4.67)	(5.53)
	(253.16613)	(5.58)	(5.57)
	(254.17054)	(4.26)	(5.92)
	(255.17383)	(5.30)	(6.16)
	(256.17861)	(3.92)	(6.47)
	(257.18211)	(5.10)	(6.87)

TABLE 3.2 *Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements (Continued)*

ELEMENT	MASS	B_n	B_p
98-Californium	(241.13899)		(3.72)
	(242.13928)	(8.10)	(3.83)
	(243.14119)	(6.59)	(4.01)
	244.14211	(7.50)	4.58
	245.14445	6.19	(4.81)
	246.14552	7.36	5.03
	247.14818	5.89	4.99
	248.14968	6.97	5.43
	249.15252	5.72	(5.59)
	250.15441	6.60	5.93
	(251.15787)	(5.15)	(6.26)
	252.16018	(6.21)	(6.65)
	253.16404	4.77	(6.75)
	(254.16665)	(5.43)	(7.10)
	(255.17097)	(4.35)	(7.18)
	(256.17383)	(5.70)	(7.59)
	(257.17844)	(4.07)	(7.74)
	(258.18182)	(5.21)	(7.85)
	(259.18675)	(3.78)	
	(260.19051)	(4.86)	
99-Einsteinium	(244.14699)		(2.18)
	(245.14738)	(8.00)	(2.68)
	246.14925	(6.62)	3.11
	247.15052	7.19	2.93
	(248.15284)	(6.20)	(3.25)
	249.15403	(7.25)	3.53
	250.15650	6.07	(3.88)
	251.15831	6.68	3.95
	252.16150	5.39	(4.20)
	253.16375	6.27	4.26
	254.16733	5.03	4.52
	(255.16987)	(6.00)	(4.58)
	(256.17368)	(4.82)	(5.06)
	(257.17649)	(5.74)	(5.10)
	(258.18073)	(4.42)	(5.45)
	(259.18386)	(5.45)	(5.68)
	(260.18846)	(4.08)	(5.99)
	(261.19179)	(5.26)	(6.39)
	(262.19717)	(3.36)	
	(263.20066)	(5.11)	

TABLE 3.2 *Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements (Continued)*

ELEMENT	MASS	B_n	B_p
100-Fermium	(245.15183)		(3.07)
	(246.15211)	(8.11)	(3.18)
	(247.15380)	(6.79)	(3.34)
	(248.15451)	(7.70)	(3.86)
	249.15664	(6.38)	(4.04)
	250.15750	7.56	4.35
	(251.15995)	(6.09)	(4.36)
	252.16124	(7.16)	4.85
	(253.16417)	(5.64)	(5.10)
	254.16615	(6.52)	5.35
	(255.16946)	(5.28)	(5.59)
	256.17151	(6.46)	(6.06)
	(257.17519)	(4.93)	(6.17)
	(258.17763)	(6.09)	(6.52)
	(259.18178)	(4.51)	(6.60)
	(260.18447)	(5.86)	(7.02)
	(261.18890)	(4.23)	(7.17)
	(262.19212)	(5.37)	(7.28)
	(263.19687)	(3.94)	(7.85)
	(264.20046)	(5.02)	(7.77)
101-Mendelevium	(248.16025)		(1.58)
	(249.16042)	(8.20)	(2.08)
	(250.16208)	(6.82)	(2.52)
	(251.16314)	(7.37)	(2.33)
	(252.16525)	(6.40)	(2.65)
	(253.16623)	(7.45)	(2.94)
	(254.16873)	(6.03)	(3.33)
	(255.17059)	(6.64)	(3.44)
	(256.17361)	(5.55)	(3.72)
	(257.17568)	(6.44)	(3.70)
	(258.17908)	(5.19)	(3.96)
	(259.18146)	(6.16)	(4.02)
	(260.18509)	(4.98)	(4.40)
	(261.18773)	(5.90)	(4.54)
	(262.19180)	(4.58)	(4.89)
	(263.19476)	(5.61)	(5.12)
	(264.19919)	(4.24)	(5.43)
	(265.20234)	(5.42)	(5.83)
	(266.20755)	(3.52)	
	(267.21087)	(5.27)	

TABLE 3.2 *Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements (Continued)*

ELEMENT	MASS	B_n	B_p
102	(249.16575)		(2.46)
	(250.16581)	(8.31)	(2.57)
	(251.16729)	(6.98)	(2.73)
	(252.16779)	(7.89)	(3.25)
	(253.16971)	(6.58)	(3.43)
	(254.17036)	(7.76)	(3.74)
	(255.17280)	(6.09)	(3.79)
	(256.17410)	(7.16)	(4.32)
	(257.17685)	(5.80)	(4.57)
	(258.17865)	(6.68)	(4.81)
	(259.18180)	(5.44)	(5.05)
	(260.18367)	(6.62)	(5.52)
	(261.18718)	(5.09)	(5.63)
	(262.18945)	(6.25)	(5.98)
	(263.19342)	(4.68)	(6.07)
	(264.19594)	(6.01)	(6.48)
	(265.20021)	(4.39)	(6.63)
	(266.20325)	(5.53)	(6.74)
	(267.20783)	(4.09)	(7.31)
	(268.21125)	(5.18)	(7.23)
103	(252.17429)		(1.06)
	(253.17426)	(8.39)	(1.56)
	(254.17572)	(7.01)	(1.99)
	(255.17657)	(7.56)	(1.79)
	(256.17864)	(6.44)	(2.15)
	(257.17957)	(7.49)	(2.48)
	(258.18191)	(6.19)	(2.87)
	(259.18359)	(6.80)	(2.98)
	(260.18644)	(5.71)	(3.26)
	(261.18833)	(6.60)	(3.24)
	(262.19156)	(5.36)	(3.51)
	(263.19377)	(6.31)	(3.56)
	(264.19723)	(5.14)	(4.03)
	(265.19970)	(6.06)	(4.08)
	(266.20359)	(4.74)	(4.43)
	(267.20638)	(5.77)	(4.66)
	(268.21064)	(4.40)	(4.97)
	(269.21363)	(5.58)	(5.37)
	(270.21866)	(3.68)	
	(271.22181)	(5.43)	

TABLE 3.2 *Isotopic Masses (Physical Scale) and Binding Energies of Last Neutron and Last Proton (in Mev) for Isotopes of Transuranium Elements (Continued)*

ELEMENT	MASS	B_n	B_p
104	(253.18044)		(1.86)
	(254.18028)	(8.51)	(1.98)
	(255.18156)	(7.17)	(2.14)
	(256.18185)	(8.09)	(2.67)
	(257.18368)	(6.66)	(2.89)
	(258.18424)	(7.84)	(3.24)
	(259.18652)	(6.24)	(3.28)
	(260.18763)	(7.33)	(3.82)
	(261.19021)	(5.96)	(4.07)
	(262.19185)	(6.84)	(4.31)
	(263.19482)	(5.60)	(4.54)
	(264.19652)	(6.78)	(5.02)
	(265.19985)	(5.26)	(5.14)
	(266.20195)	(6.41)	(5.49)
	(267.20574)	(4.83)	(5.58)
	(268.20810)	(6.17)	(5.99)
	(269.21219)	(4.55)	(6.14)
	(270.21506)	(5.69)	(6.25)
	(271.21947)	(4.26)	(6.82)

of the neutron, 1.00898, and energy equivalent of mass, 931.14 Mev per atomic mass unit.

The method and the fundamental data outlined in the past few paragraphs were used to calculate the atomic mass values summarized in Table 3.2. In this table, uncertain values are given in parentheses. Proton- and neutron-binding energies were calculated for each isotope from the mass values using the value 1.00898 for the mass of the neutron and 1.00814 for the mass of the proton.

3.3 Alpha- and Beta-Decay Energies

The alpha- and beta-decay data, including the energies and the half lives of the transitions, are of the greatest importance to this region. These data, together with the gamma-ray data, are the basis for determining the energy levels of these nuclides, which will be discussed to some extent below. We shall first discuss the regularities in the alpha- and beta-decay data—that is, the systematics of such decay. A brief table summarizing the radioactive decay data for the transuranium nuclides is given in the Appendix.

Fig. 3.12 is a plot of alpha-decay energy versus mass number

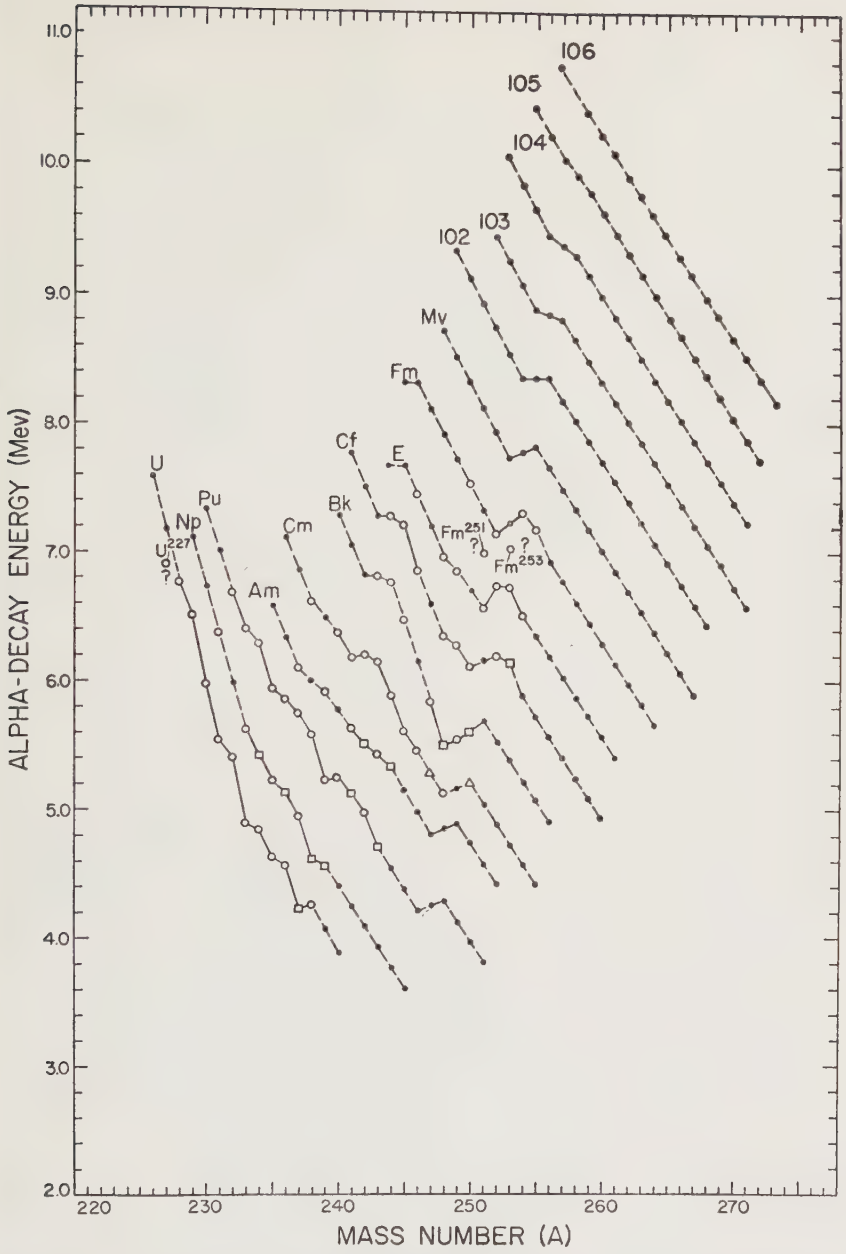
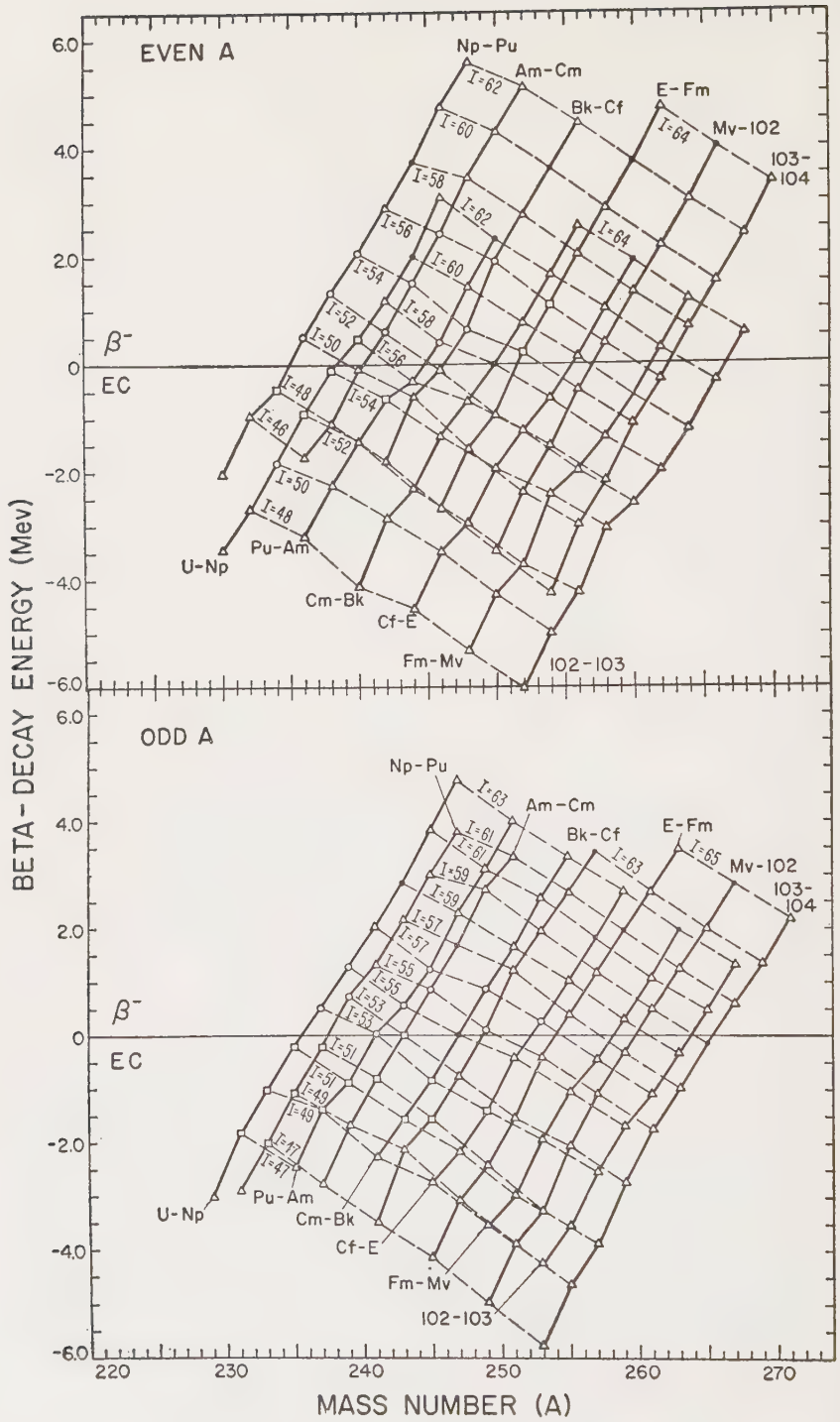


Fig. 3.12 Alpha-decay energies for the isotopes of the transuranium elements as a function of mass number. Meaning of symbols: ○ experimental value; □ calculated value; ● estimated value; △ calculated from a cycle containing estimated energies; ?, total decay energy in question.


EVEN A
ODD A
Np-Pu
Am-Cm
Bk-Cf
E-Fm
Mv-102
103-104
U-Np
Pu-Am
Cm-Bk
Cf-E
Fm-Mv
102-103
β⁻
EC
BETA-DECAY ENERGY (Mev)
MASS NUMBER (A)
6.0
4.0
2.0
0
-2.0
-4.0
-6.0
220
230
240
250
260
270

where the points representing a given element have been connected. The decay energy refers to the ground-state transition and includes the nuclear recoil energy in addition to the energy of the alpha particle. Except for minor irregularities, the alpha energies for isotopes of a given element generally decrease in a regular fashion with increasing mass number. This finds a logical explanation in the shape of the energy surface in this region and in the fact that alpha-particle emission changes the mass of the emitter by only four mass units for a change in atomic number of two units. Extensions of the experimental curves make it possible to predict unmeasured or unmeasurable disintegration energies between or beyond the measured ones.

In the curves showing experimental values for the elements californium, einsteinium, and fermium, an irregularity occurs which reflects a discontinuity of the energy surface in this mass region. The simple shell model of the nucleus shows a large discontinuity in nuclear properties for isotopes in the region of 126 neutrons, since, according to this model, 126 neutrons represent a completely filled major shell. The alpha-disintegration energies for isotopes below the transuranium element region show a striking discontinuity of 3 to 4 Mev in the mass region which includes isotopes on both sides of the 126-neutron shell. The discontinuity which appears in Fig. 3.12 is of a much smaller magnitude and has been ascribed to a sort of "subshell" closure at 152 neutrons by Ghiorso, S. G. Thompson, G. H. Higgins, B. G. Harvey, and the author; such a subshell closure is not predicted from a simple consideration of the shell model. (As has been pointed out by F. Asaro, F. S. Stephens, Jr., and I. Perlman, there seems also to be a very small jog in some of the curves corresponding to nuclides with 145 neutrons, perhaps indicating some small extra stability in this neighborhood.)

In the case of elements beyond element 100, for which no ex-

Fig. 3.13 Beta-decay energies for the isotopes of the transuranium elements as a function of mass number. Points for nuclides undergoing the transition $Z \rightarrow Z \pm 1$ are connected with solid lines and points for nuclides with equal values of $I (= A - 2Z)$ are connected with dotted lines. Meaning of symbols: ○ experimental energy; □ calculated energy; ● estimated energy; △ calculated from a cycle containing estimated energies. Upper part of figure refers to even mass types. Lower part refers to odd mass types.

perimental points are available, lines have been placed in Fig. 3.12 after due consideration of the spacings and slopes of the lines for elements 98, 99, and 100, including an allowance for a probable break at 152 neutrons. Values taken from these lines are probably subject to more error than values taken from an extension of the curves for lower elements. Data taken from the curves of Fig. 3.12 were used in the construction of the decay energy cycles of Figs. 3.8 to 3.11.

In Fig. 3.13 the beta-decay energies for the transuranium element isotopes have been correlated with mass number. The upper part of the figure presents the data for even-mass types; the lower part refers to the odd-mass types. Similar curves have been given by K. Way and M. Wood and by H. E. Suess and J. H. D. Jensen. The legend distinguishes those decay energies which are directly measured, those which are estimated, those calculated by closure of suitable decay cycles in Figs. 3.8 to 3.11, and those calculated from decay cycles involving estimated alpha-decay energies taken from Fig. 3.12. Directly measured decay energies involve a knowledge of the decay scheme as well as of the maximum energies of the beta particle groups. In many instances, unfortunately, the decay scheme is not known with certainty.

From Figs. 3.8 to 3.11 it is possible to determine which transuranium element isotopes are stable toward the emission of negative beta particles and the capture of orbital electrons—that is, the

TABLE 3.3 *Beta-Stable Isotopes of Transuranium Elements*

Neptunium	Np^{237}
Plutonium	Pu^{236}, Pu^{238}, Pu^{239}, Pu^{240}, Pu^{242}, Pu^{244}
Americium	Am^{241}, Am^{243}
Curium	Cm^{242}, Cm^{244}, Cm^{245}, Cm^{246}, Cm^{247}(?), Cm^{248}, Cm^{250}(?)
Berkelium	None
Californium	Cf^{248}, Cf^{249}, Cf^{250}, Cf^{251}, Cf^{252}, Cf^{254}, Cf^{256}(?)
Einsteinium	E^{253}
Fermium	Fm^{252}, Fm^{254}, Fm^{255}, Fm^{256}, (Fm^{257}), (Fm^{258}), (Fm^{260}(?)), (Fm^{262}(?))
Mendelevium	(Mv^{259})
102	(102^{258}), (102^{260}), (102^{261}), (102^{262}), (102^{263}), (102^{264}), (102^{266})
103	(103^{265})

(parentheses enclose unknown isotopes predicted to be beta stable; a question mark indicates an isotope for which the uncertainties in the data make it impossible to be sure of its beta stability)

nuclides which are "beta stable." This important information is summarized in Table 3.3. Further estimations concerning such nuclides are shown in Fig. 4.8 of Chapter 4.

3.4 Discussion of Unified Nuclear Model

Since the discussion in the following sections of nuclear energy levels and alpha-, gamma- and beta-decay rates in the heaviest elements will lean heavily on the applicable unified nuclear model, this section will be devoted to a brief discussion of the main features of this model.

The nuclear shell model of M. G. Mayer and O. Haxel, J. H. D. Jensen, and H. E. Suess considers the motions of unpaired nucleons in an average nuclear field generated by the other nucleons in the nucleus. This average nuclear field is assumed to be isotropic and is mathematically approximated by a square well, an infinite harmonic oscillator potential, or by some special potential related to these. In addition, spin-orbit coupling has to be assumed if the correct orbit levels are to be obtained.

In this simple, single-particle model the spectroscopic state of an odd-A nucleus is determined by the odd nucleon. The spin, s, and the orbital angular momentum, l, of this odd nucleon combine to give j, the total angular momentum, which in nuclear parlance is the nuclear spin, I, of the ground or excited states. The parity of the nucleus is positive or negative according to whether the value of l of the odd nucleon is even or odd. All of the nucleons are paired in the ground states of even-even nuclei, leading to zero spin and positive parity, and excited states result from unpairing and lifting of nucleons to higher levels. More complicated considerations are involved in determining the spectroscopic states of odd-odd nuclides (containing both an odd proton and an odd neutron) and of nuclides in general where the interactions of two or more unpaired nucleons are important. Major closed shells are obtained by the theory, and are experimentally found, in nuclides containing 2, 8, 20, (28), 50, 82, protons and neutrons and 126 neutrons.

Since the average nuclear field is generated by the nucleons, it is to be expected that collective oscillations of the nucleus will change the potential experienced by the odd nucleon and perturb

the energy levels. A. Bohr, in particular, has developed a theory exploring the consequences of interaction of single particle and collective motions of the nucleus. This theory is frequently referred to as the Unified Model. Bohr's theory has been further developed by A. Bohr and B. R. Mottelson and their collaborators at Copenhagen. D. L. Hill and J. A. Wheeler have independently developed a unified model along somewhat different lines.

In the heavy element region the nuclei in the region of Pb^{208} can still be treated successfully by the simple shell model. Thus Pb^{208} has a closed shell of protons (82) and a closed shell of neutrons (126). Nuclei in this region strongly prefer spherical symmetry and are so stiff toward shape changes that collective motions are not very important in the prediction of properties of the ground state and low-lying states. For nuclei a few nucleons removed from Pb^{208}, the shell model treatments of M. H. L. Pryce (cf. also D. E. Alburger and Pryce) and of W. W. True treating specific nucleon-nucleon interactions among the nucleons outside the closed shells are of greatest utility.

On the other hand, in the region of the heaviest elements, starting roughly at neutron number 138 and going up to the heaviest nuclei yet studied, the simple shell model is not applicable and the unified model is very successful in correlating nuclear properties. In this group of nuclides the preferred nuclear shape is not spherical but spheroidal. Nuclei in the region of neptunium and plutonium, for example, are about 25 per cent longer along the principal axis of the spheroid than along the minor axes. For nuclei which are thus stabilized in a nonspherical shape, rotational and vibrational level structures are to be expected for each intrinsic particle state. The description of these motions requires a number of new quantum numbers, which will be briefly discussed.

In the intermediate region between the Pb^{208} region (spherical nuclei) and the heaviest elements (spheroidal nuclei) there is a transition region where the nuclei are most stable in a spherical shape but are soft toward collective vibrations. The mathematical treatment for this region is more difficult to carry out, and it has not been possible to give as satisfactory a description of the observed nuclear states, although a few special classes of vibrational spectra in even-even nuclei have been treated by G. S. Goldhaber and

J. Weneser and by L. Wilets and M. Jean. Since our main interest here is in the transuranium element region we shall not say anything further about this intermediate group of nuclei.

Returning to the region of the transuranium elements, we shall discuss some of the quantum numbers that are useful for the description of the energy states, even though it is beyond the scope of the present discussion to give a complete description of the model which is employed; this nomenclature will be used in some of the discussion and illustrative diagrams to follow. The spectrum for such a strongly deformed nucleus involves states corresponding to three types of excitation; these are the intrinsic particle excitations and the collective vibrational and rotational excitations. A great simplification can be made in the mathematical treatment because the interactions of these three types of excitation are relatively small and thus to a first approximation they can be treated independently of each other.

The first mode of excitation corresponds to the state of the particle motion with respect to the deformed field and is characterized by the quantum number Ω, defined as the component of the total nucleonic angular momentum along the nuclear symmetry axis for the spheroidal nucleus; the energies involved in such excitations are determined by the positions of the particle levels in a spheroidal field which have been calculated by S. G. Nilsson and others and will be discussed further below. The average spacing is about 100 Kev. The single particle total angular momentum j (so important in the simple shell model classification of states) is not, in general, a constant of motion for the deformed potential. The second mode of excitation is associated with collective vibrations; the state of vibration with retention of spheroidal symmetry is specified by the quantum number, n_β, and that with change from spheroidal symmetry is specified by the quantum number, n_γ. The quantum energy of these excitations (quadrupole vibrations) is expected to be about one Mev. The third mode of excitation is associated with nuclear rotation with preservation of shape. The quantum numbers I and K characterize the whole system, I being the total angular momentum (or nuclear spin) of the nucleus, and K the component of total angular momentum along the symmetry axis. The state of rotation is implicitly defined by I and K. The

nucleus rotates about an axis perpendicular to the symmetry axis, from which it follows that I for a given state is never less than K. For all states not involving vibrations and for the beta ($n_\beta \neq 0$, $n_\gamma = 0$) vibrational states K is equal to Ω; this will be the situation for nearly all cases we consider here. The beta vibrational states have $K = 0$ while the first gamma ($n_\gamma = 1$) vibrational state has $K = 2$; the latter asymmetric mode of vibration can thus in a sense be considered to have a rotational component. The rotational motions are easily excited, with the level spacings governed by a simple relationship given below on page 228. The rotational energies depend on the degree of nuclear deformation and the energy of the first state (about 50 Kev) becomes much smaller than the vibrational energies for the strongly deformed nuclei.

Even-even nuclei have the rotational sequence 0+, 2+, 4+, 6+ . . . . (that is, total nuclear angular momenta in the sequence 0, 2, 4, 6 . . . and each state with even parity) based on an 0+ intrinsic ground state. (For an even-even nucleus in the ground state all nucleons are paired and $K = \Omega = 0$.) Rotational levels may also be based on vibrational levels or excited nucleonic levels. As an excited nucleonic state always corresponds to the breaking of a pair, such states are seen first at excitations of about one Mev. Thus most of the low-lying levels in heavy even-even nuclei represent rotational or vibrational structure based on the 0+ intrinsic ground state.

For nuclei with odd mass numbers or for odd-odd nuclei, excited particle states may also be expected in low-lying levels, and these may be the base for rotational structure. Nuclei with odd mass numbers have rotational bands with spin sequences K, $K + 1$, $K + 2$, etc., with the same parity as that of the state on which the sequence is based. The parity, π, is determined as positive or negative according to whether the l-value of the odd nucleon orbital is even or odd when traced back to zero deformation on a "Nilsson diagram" (to be discussed below).

The above-described simple separation of the spectra represents a limiting case; for the less-deformed nuclei the more rapid rotational motion will somewhat distort the shape of the nucleus and will also perturb the particle structure, because of the inability of the particles to follow the rotations completely adiabatically.

In more detailed applications of the model for deformed nuclei, attempts are made to understand transition rates and magnetic moments in terms of intrinsic nucleonic structure within the deformed well. Single-particle wave functions in a spheroidal well are useful for such applications. Again, it is worth-while to introduce some of the concepts involved here (even though it is beyond the scope of the present discussion to give a complete description of the method) because the nomenclature will be used, although only in a supplementary way, in some of the illustrative material to follow. In order to further classify nucleonic states S. G. Nilsson has suggested for use at large deformations the asymptotic quantum numbers, N (total oscillator quantum number), n_z (symmetry axis oscillator quantum number), Λ (nucleonic orbital-angular momentum component along the symmetry axis), and Σ (nucleonic spin-angular momentum component along the symmetry axis). Thus Λ plus Σ must equal Ω, the total nucleonic angular momentum along the nuclear symmetry axis. The violation of selection rules in these quantum numbers for beta and gamma transitions appears generally to have a retarding effect on transitions, although not so severe as a violation of K-selection rules (defined below). Fig. 3.14 shows a plot of eigen values for a nucleon (neutron) in a prolate spheroidal three-dimensional harmonic oscillator potential with strong spin-orbit coupling, according to the calculations of Nilsson. The levels are labeled in the ordinary shell-model convention corresponding to a spherical well, according to l and j given at the left of the figure. At the right-hand (and top) side, corresponding usually to large values of the prolate deformation parameter, δ—defined as the difference of radii along the symmetry axis and the perpendicular axis divided by the radius of a sphere of the same volume as the spheroid $\left(\delta = \frac{R_{\parallel} - R_{\perp}}{R_o}\right)$—the levels are labeled according to the Ω-quantum number and the parity, π, of the level. (The value for δ can be estimated in various ways, such as from the quadrupole moment of the nucleus, which, in turn, can be determined experimentally in a number of ways.) The Ω value is generally equal to the nuclear spin I of the lowest energy state of the band associated with that Nilsson orbital, except that for $\Omega = 1/2$ spins other than $1/2$ may lie lowest. In parentheses are

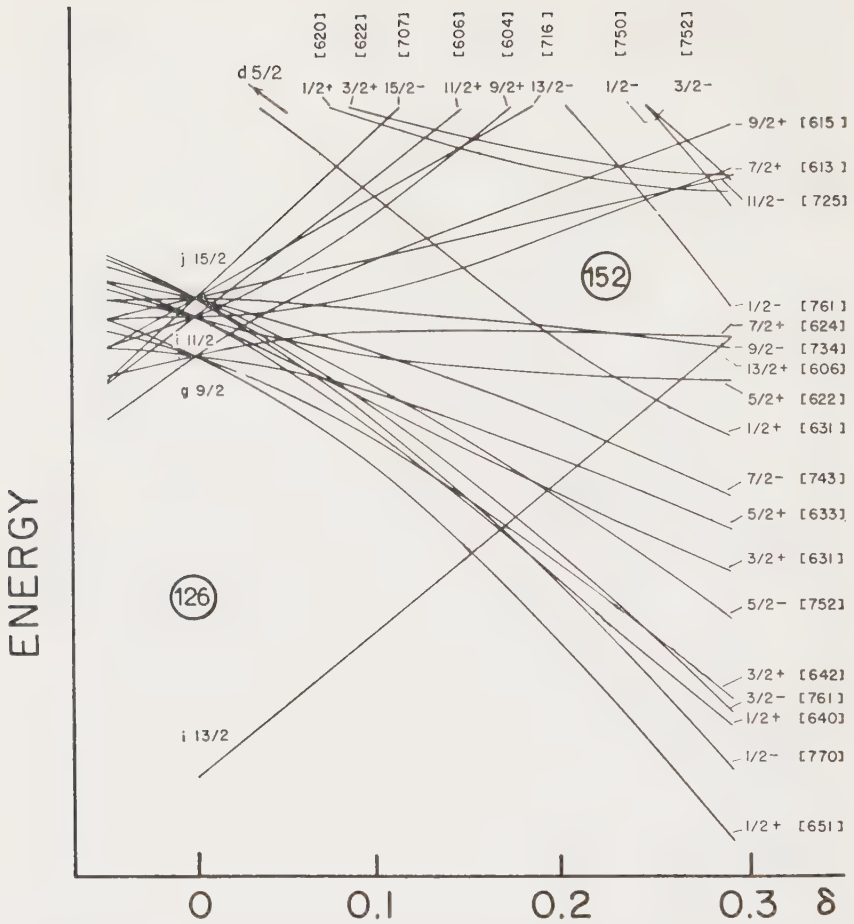


Fig. 3.14 Plot of eigenvalues for a neutron in a prolate spheroidal three-dimensional harmonic oscillator potential with strong spin-orbit coupling according to the calculation of S. G. Nilsson.

The levels are labeled in the ordinary shell model convention, according to l and j at the extreme left of the figure, corresponding to a spherical well. At the right hand side (and top) the levels are labeled according to the Ω quantum number (the spin I of the base state of a nuclear rotational band except in some cases for $\Omega = 1/2$) and the parity of the level; in parentheses are the asymptotic quantum numbers N, n_z and Λ most appropriate to the eigenfunction at the largest deformation ($\delta = 0.3$) here plotted.

the asymptotic quantum numbers, N, n_z, and Λ. The asymptotic quantum number Λ can be determined as follows: Λ can differ from Ω only by 1/2 and takes the even or odd value according to whether $N - n_z$ is even or odd. The level scheme accounts fairly well for the observed sequence of spins and magnetic moments and is also consistent with a rather natural gap in levels at large deformation for 152 particles, thus offering some rationale for the observed neutron "subshell" at 152. Fig. 3.15 shows a similar "Nilsson diagram" for protons.

At this point it may be appropriate to review the quantum numbers introduced in our discussion of the unified model.

These quantum numbers may be classified in three categories:

First there appear the model-independent quantum numbers I and π, the total nuclear angular momentum (spin) and parity.

The second group of quantum numbers includes K, the component along the nuclear symmetry axis of the angular momentum of the total system, and Ω, the corresponding component of the angular momentum of the nucleonic, intrinsic motion. For all cases, except when γ-vibrational modes are excited, K is equal to Ω. The validity of these quantum numbers depends on the assumption of the separability of the different modes of motion (or applicability of the adiabatic coupling scheme). The quantum numbers n_β and n_γ should also be included in this group, where n_β and n_γ are the quantum numbers corresponding to vibrations that preserve and do not preserve, respectively, rotational symmetry.

The third group of quantum numbers is even more dependent on the specific properties of the model. These are the so-called asymptotic quantum numbers, which are of a more approximate character than the quantum numbers of the second group. Included are the quantum numbers N, the total number of oscillator quanta characteristic of a nucleonic state, and n_z, the number of quanta along the nuclear symmetry axis. To this group belong also the quantum numbers Λ and Σ, the components along the symmetry axis of the orbital angular momentum and intrinsic spin, respectively, of a particular nucleonic state.

These quantum numbers are all useful in correlating nuclear data corresponding to decay spectra. Relations involving only I and π will not particularly concern us here. It may be pointed out,

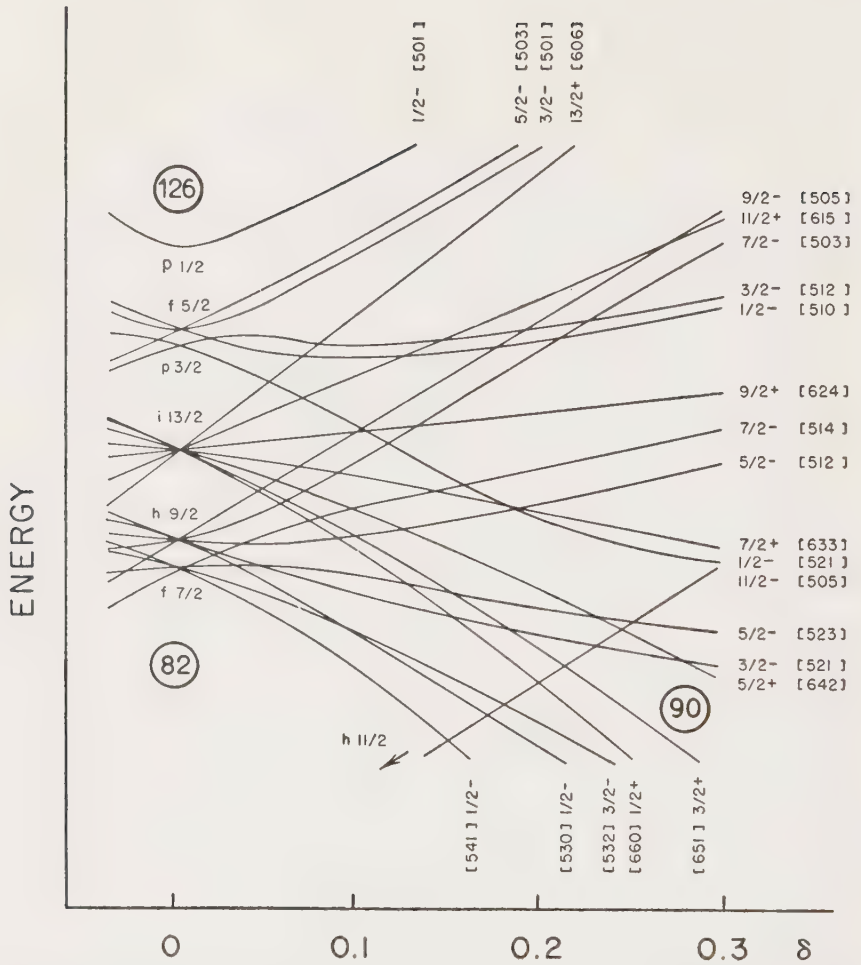


Fig. 3.15 Plot of eigenvalues for a proton in a prolate spheroidal three-dimensional harmonic oscillator potential with strong spin-orbit coupling according to the calculation of S. G. Nilsson.

The levels are labeled in the ordinary shell model convention, according to l and j at the extreme left of the figure, corresponding to a spherical well. At the right hand side (and top and bottom) the levels are labeled according to the Ω quantum number (the spin I of the base state of a nuclear rotational band except in some cases for $\Omega = 1/2$) and the parity of the level; in parentheses are the asymptotic quantum numbers N, n_z and Λ most appropriate to the eigenfunction at the largest deformation ($\delta = 0.3$) here plotted.

however, that there are many features of empirical data that can be correlated solely on the basis of the quantum numbers of the first two groups without invoking the third group. There exists, for example, a selection rule for emission in which a unique total angular momentum L is carried off—that is, in gamma transitions or in beta transitions of the so-called unique type (where the β-ν pair is sent out with a unique total angular momentum L equal to the order of forbiddenness plus one), or in alpha transitions—stating that L has to be equal to or greater than ΔK. The violation of this rule corresponds empirically to one or several orders of magnitude of delay in emission rate. This "K-selection rule" is easily understood on the basis of simple vector considerations. The rule merely expresses the fact that the angular momentum carried off by the ejected particle(s) (or gamma quantum) has to at least equal the change of nuclear angular momentum ΔK along a specific direction. (The length of a vector is at least equal to any of its components.)

As pointed out, a so-called rotational band of energy levels corresponds to states displaying the same intrinsic nucleonic structure, but the different individual levels represent different frequencies of rotation. The relative population of such states by transitions characterized by a definite L value (removing the energy dependence) will be dependent only on structure-independent quantities, simple vector-coupling, or Clebsch-Gordan, coefficients involving I and K of the initial and final states and dependent on L. The application of this rule implies that the values of I and K are known, but the rule may be employed the other way around to decide, for example, between the different possible K values.

From a knowledge of the intrinsic structure (that is, the nucleonic wave functions) one may predict a likely value of Ω or K of the nuclear ground state and of excited nucleonic levels. With a knowledge of the ground-state Ω, the nuclear spin is determined from the relation $I = \Omega$, a relation that is valid except when $\Omega = 1/2$, in which case a more detailed knowledge of the nucleonic wave function is required to decide the I value of the ground state.

In analyzing empirical decay schemes, experience has shown that instead of applying the detailed nucleonic wave functions, one can retain most of the information by just assigning the so-called

asymptotic quantum numbers N, n_z, Λ, and Σ to the nucleonic states identified in the decay scheme. It must be emphasized that the applicability of these latter quantum numbers implies not only the fulfillment of the conditions required for the second group of quantum numbers (adiabatic coupling scheme) but, in addition, the applicability of a single particle description for the nucleons and some restrictions on the choice of the average nuclear potential. Finally, it is also required that the eccentricity of the nuclear shape shall be so large that the effect of the spin-orbit term in the nuclear potential is much smaller than the effect of the deformation. The beta and gamma transitions are governed by selection rules restricting excessive changes in these quantum numbers. For more information on the detailed character of these selection rules the reader is referred to the sections on gamma- and beta-decay rates (Tables 3.7 and 3.10). However, as a weaker form of these selection rules one might state that none of the quantum numbers is allowed a greater change than that which corresponds to the total angular momentum, L, carried off in the emission process.

3.5 Alpha-Decay Rates

A substantial amount of progress has been made in understanding and correlating alpha-decay rates. The initial conception by G. Gamow and by E. U. Condon and R. W. Gurney of the alpha-decay process as a barrier penetration problem has been cast into a number of forms differing in detail but basically all ending with the decay rate expressed as the product of two factors: (a) a "frequency factor" which may be considered as the decay rate without the barrier; and (b) a "penetration factor" which expresses the probability of an alpha particle emerging through the negative energy region of the Coulombic potential barrier. The alpha particle is treated as existing in the "preformed" state in the simple one-body theory. The various solutions to the problem differ in the degree of rigor which is applied, and it might be stated that the sensitive portion is the "penetration factor," which is exponential in form and is similar in the several treatments. The parameters which enter into the penetration factor are those which define the barrier for the alpha particle of energy E, and these are the nuclear

charge and the effective nuclear radius. The frequency factor, likewise, may be a function of the energy of the alpha particle and nuclear radius, but we do not know at present just what to assume for it. However, consistent correlations with data are obtainable for wide variation of values assumed for the frequency factor, if the "effective nuclear radius" is allowed as a parameter to be fixed by the choice of frequency factor. It is interesting to note that spin change in itself does not affect alpha-decay rates as much as was previously postulated, although related effects are important, as the discussion below will show. Alpha particle angular momentum, L, leads to a centrifugal barrier reduction of the penetrability, but if one takes the one-body (alpha in a potential well) theory quite literally there is a counter tendency for the frequency factor to increase with L. The net effect is a slightly increased rate for small values of L, and the net rate does not decrease until L is greater than four.

There are, of course, some strict selection rules for alpha decay based on conservation of total angular momentum and parity. Thus we have $|I_i - I_f| \leq L \leq I_i + I_f$ where I_i and I_f are the nuclear spins (total angular momenta) of the initial and final nuclear states. Only even values of L are allowed if the parity (π) of the initial and final nuclear states is the same, and only odd values of L are allowed if there is a parity change. If either I_i or I_f is zero, it is possible to have cases where alpha decay is strictly forbidden. For example, alpha decay of an even-even nucleus ($0+$) cannot populate odd spin states of even parity, or even spin states of odd parity.

Fig. 3.16 shows a plot of the half life versus energy relationship as a family of curves for even-even alpha emitters. The dotted lines correspond to the predictions for elements 102, 104, and 106. The solid curves are defined by the experimental half lives and are, in this respect, empirical. If, however, we were to calculate half lives according to modern alpha-decay theory, by using the measured alpha energy for each point and assuming the function for the nuclear radius, $1.5 \times 10^{-13}A^{1/3}$, the resulting curves would lie close to those of Fig. 3.16. The relative probabilities of the ground-state transitions of even-even alpha emitters are treated with extraordinary precision by basic one-body, alpha-decay theory. However, analysis of the many alpha spectra obtained during

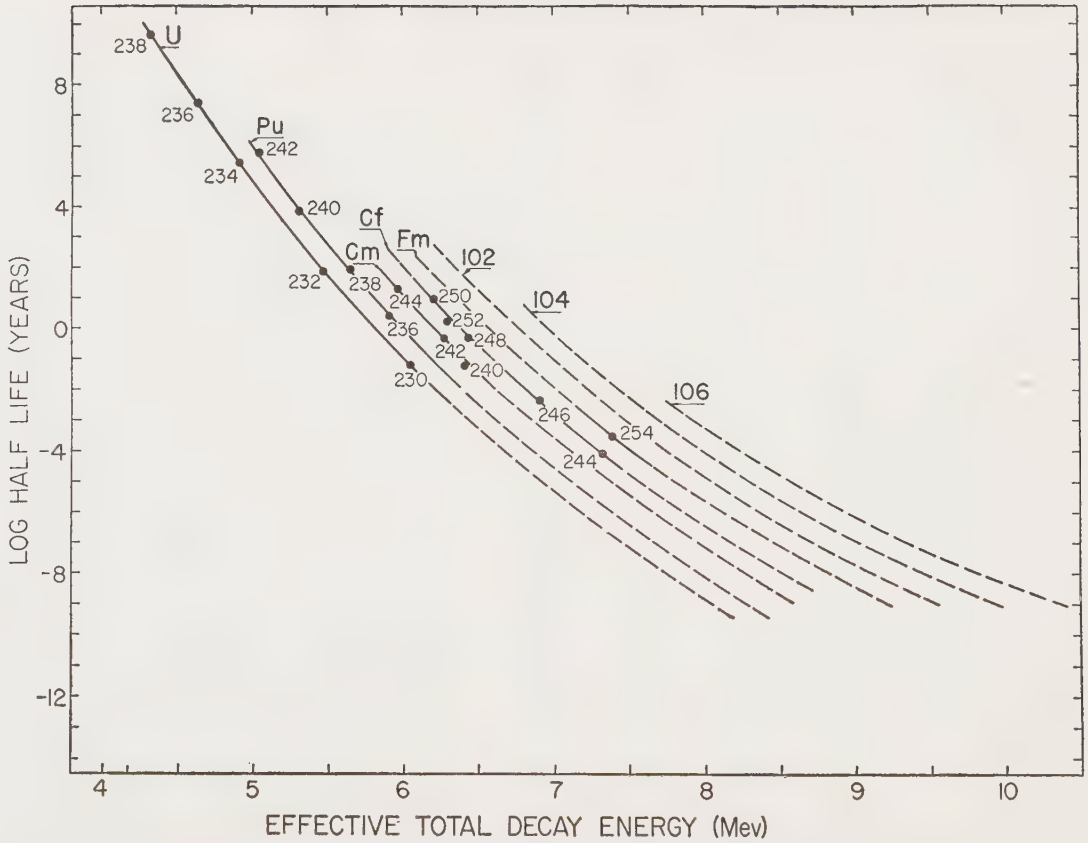


Fig. 3.16 Half life of even-even isotopes versus alpha-decay energy.

the past few years has shown clearly that more elaborate theory is required to account for the behavior of other nuclear types, as well as for certain of the transitions to excited states of the even-even nuclei.

Two points should be mentioned with respect to the curves of Fig. 3.16. It may be noted that the energy values listed are somewhat higher than measured particle energies. The alpha energy entering into alpha-decay theory is the total disintegration energy; therefore, the particle energy must be increased by the energy of the recoil nucleus. This correction amounts to ~100 Kev for a 6-Mev alpha particle in this region. An additive correction to the alpha particle energy which has been long overlooked has been suggested by G. Ambrosino and H. Piatier and has to do with the lowering of the potential barrier by the electron cloud. As pointed out by J. O. Rasmussen, this orbital electron "screening" correction should be applied as an added alpha energy amounting to about the difference of total electron-binding energies between parent and daughter in the particular alpha-decay process. This amounts to ~38 Kev in this region.

The odd-nucleon alpha emitters, especially in the ground-state transitions, decay at a slower rate than that suggested by the simple one-body formulation as applied to even-even nuclei. This means that the points representing the decay data for such nuclides would lie above the lines shown in Fig. 3.16, or for odd-atomic-number nuclides the points would lie above the hypothetical interpolated lines. These are referred to as hindered decays, and the "hindrance factor" may be defined as the ratio of the measured partial half life for a given transition to the half life which would be calculated from simple, one-body, alpha-decay theory as applied to even-even nuclei. Although a quantitative theoretical explanation has not yet been formulated, one suggestion put forward by I. Perlman, A. Ghiorso, and the author has to do with the breakdown of the one-body model in its implication that the alpha particles to be emitted exist as discrete entities within the nucleus; the one-body model suggests that the probability of alpha emission depends only upon the frequency factor of this preformed alpha particle in encountering the Coulomb barrier and upon the rate of barrier penetration. For ground-state transitions of even-even nuclei the simple

one-body rate formulations are satisfactory, implying that the fraction of time the most lightly bound nucleons spend in an alpha particle cluster does not vary greatly from nucleus to nucleus. For ground-state transitions of odd-nucleon emitters and in certain other transitions, however, it is suggested that there can be a considerable time involved in assembling the components of the alpha particle. The odd nucleon, presumably the one in the highest quantum state, must be a component of the emitted alpha particle if the alpha particle is to leave the nucleus with full kinetic energy; as a result it must, in effect, pair with a lower-lying nucleon already paired with another nucleon and perhaps in addition one or more of the remaining nucleons may have to change quantum states. However, a more favorable case corresponds to forming the alpha particle by using lower-lying pairs, leaving the odd nucleon in its initial orbital. In this case the state of the remaining nucleus usually corresponds not to the daughter ground state but to an excited state; this excited state is then characterized by the same orbital as that of the ground state of the emitting nucleus. Only for those transitions where the odd-particle wave function remains unaltered would one expect unhindered (sometimes referred to as "favored") alpha decay. Significantly, it appears that such transitions can be found in the spectra of the odd-nucleon emitters, and, as expected, these are, in general, not the ground-state transitions.

These simple considerations can be developed further on the basis of the unified model. The decay scheme of Am^{241} leading to Np^{237}, shown later in Fig. 3.21, may serve as a detailed illustration. The Am^{241}, with ground-state unified-model quantum designations $I = K = 5/2$, $N = 5$, $n_z = 2$, $\Lambda = 3$, $\pi = -$, decays mainly (corresponding to a hindrance factor equal to about one) to the 59.57-Kev state of Np^{237}, with identical quantum designations. On the other hand the decay to the ground state of Np^{237}, with quantum numbers $I = K = 5/2$, $N = 6$, $n_z = 4$, $\Lambda = 2$, $\pi = +$, has a hindrance factor greater than 500.

The decay scheme of Am^{241} shown in Fig. 3.21 can be further used to illustrate another interesting feature, applicable to odd-A nuclides, that is rather well understood on the basis of the unified model as pointed out by A. Bohr, P. O. Fröman, and B. R. Mottelson. Based on the 59.57-Kev state with spin 5/2 there occurs a

rotational band, the levels of which are denoted as B 7/2, B 9/2, etc., the numbers 7/2 and 9/2 referring to the total angular momentum (nuclear spin, I) values. The alpha population to these states varies after a characteristic pattern, rapidly decreasing with increase of I. The relative alpha population to these states seems to be calculable and depends only on (1) the energy of decay to the excited states, (2) the angular momentum associated with the alpha decay, and (3) certain geometric factors (vector-coupling, or Clebsch-Gordan, coefficients). This is plausible, since all these states according to the unified model are associated with the same intrinsic nucleonic structure. The energy dependence (1) of the decay to the excited state can be approximately determined from the relationship involving the parameters, A_z and B_z, given later in this section. For these "favored" transitions the explicit dependence on angular momentum (2), which includes the interaction of the outgoing alpha waves with the quadrupole moment of the nucleus, is assumed for the odd-nucleon emitters to be the same as found experimentally for nearby even-even alpha emitters. The geometrical factors (3) are simple functions of the I and K quantum numbers (the total angular momentum and its component along the nuclear symmetry axis) of the involved states and, in addition, the angular momentum L carried off by the alpha particle.

The alpha decay of Am^{241} to the rotational band based on the 59.57-Kev level, displaying hindrance due mainly to the penetration factor, is an example of no change in intrinsic particle states and hence ΔK equals zero (and, of course, no change in parity). The alpha decay of Am^{241} to the daughter ground state, displaying hindrance due to both penetration and frequency factors, is an example of a change in the intrinsic particle states with ΔK equal to zero and a change in parity. Also, we may have change in the intrinsic particle states with ΔK not equal to zero (but perhaps still with no change in I), which also introduces hindrance due to both frequency and penetration factors. In the case where there is a change in K or parity, the alpha particle will have to carry an angular momentum different from zero which will affect the penetration factor; the change in K or parity implies a radical change of the odd-nucleon orbital between initial and final states, which can cause a delay in the formation of the alpha particle and an effect on the

frequency factor which varies from small to very large. The Cm^{243} decay to Pu^{239} provides an example where ΔK is not equal to zero with no change in parity (Fig. 3.23). There the Cm^{243} ground state is characterized by $I = K = 5/2$, while the 57.31-Kev level in Pu^{239} is classified as $I = 5/2$, $K = 1/2$. The transition is empirically very hindered. There is also the possibility, for which we quote no example, of alpha decay with ΔK equal to zero and no change in parity, leading to little effect on the penetration factor but with a change in intrinsic particle states, leading to hindrance due to the frequency factor.

L. D. Landau has given a simple formula for highly prolate nuclei which emit practically all alpha particles from a narrow region surrounding the major semi-axis. He feels that this is valid for even-even and odd-A nuclides, for calculating the relative alpha populations, P, to a band of rotational levels. His formula has the form:

$$P = C(2I + 1)e^{-\alpha I(I+1)}$$

where C and α do not depend on the energy levels and can be theoretically related to the dimensions and eccentricity of the nucleus. K. A. Ter-Martirosian has proposed a more complicated formula applicable to odd-A nuclei. Along quite different lines L. A. Sliv has made calculations of the probability for alpha decay for a nucleus executing surface oscillations with an amplitude depending on the number of nucleons outside a closed shell and with a distribution function for alpha particles on the surface that has a maximum where there is deformation. These considerations have not been tested in any detail at the time of the present writing.

In calculating the hindrance factor, F, defined as the ratio of the measured partial half life for a given alpha transition to the half life which is calculated from simple, one-body, spin-independent, alpha-decay theory, a simple mathematical definition, in terms of a simple analytical expression, is useful. C. J. Gallagher and J. O. Rasmussen, and A. Bohr, P. O. Fröman, and B. R. Mottelson suggest such an expression based on the formulation that the logarithm of the alpha half life should be equal to $A_z Q_{\text{eff}}^{-1/2} + B_z$, on the basis of simple alpha-decay theory, where A_z and B_z are constants for a given atomic number and Q_{eff} is the total alpha-decay energy in million electron volts (alpha particle

energy plus recoil energy plus the "screening" correction). Thus the hindrance factor, F, for an alpha group of an even-odd nucleus can be obtained by substituting that group's partial half life ($t_{1/2\alpha}$) and Q_{eff} into the expression $\log_{10} F = \log_{10} t_{1/2\alpha} - A_z Q_{\text{eff}}^{-1/2} - B_z$, with A_z and B_z for that particular element being used. The decay rate data for ground-state groups of even-even isotopes for each even atomic number element should be separately used to determine by least-squares fitting the best values for the constants A_z and B_z. The hindrance factors for odd-even and odd-odd alpha emitter groups are to be calculated by using for A_z and B_z the arithmetical mean of the corresponding values for the two adjacent even atomic numbers. The hindrance factors to excited states of an even-even nucleus are given a special definition to make the basis of comparison its own ground-state transition; that is, the hindrance factor for even-even nuclei is equal to the F value calculated for the excited-state group divided by the F value similarly calculated for the ground-state group. The constants A_z and B_z, determined by Gallagher and Rasmussen by least-squares analyses of the data for even-even alpha emitters, are listed in Table 3.4; the units of $t_{1/2\alpha}$ are seconds. The values for einsteinium and fermium were obtained by extrapolation.

TABLE 3.4 *Semi-Empirical Constants for Hindrance-Factor Calculations*

ELEMENT	A_z	B_z
100 Fm	156.38	−53.3742
99 E	155.04	−53.3141
98 Cf	152.86	−52.9506
97 Bk	152.65	−53.3166
96 Cm	152.44	−53.6825
95 Am	149.33	−52.8862
94 Pu	146.23	−52.0899
93 Np	146.86	−52.8732

This equation is strictly applicable to ground-state transitions whose mass-energy relations are the same as for ground-state transitions of even-even nuclides. Thus an error will be introduced in the calculation of F values for transitions to excited states. For transitions to excited states of less than 100-Kev energy, the error will be less than 10 per cent.

The hindrance factors for all alpha transitions where the partial

half life and energy are known can, of course, be tabulated. It is beyond the scope of this present book to include such detailed tabulations of data, but some of the decay schemes that are presented later will give some notion of the erratic way in which the hindrance factors vary for odd-nucleon alpha emitters. However, there are an increasing number of correlations appearing as the data accumulate and are analyzed. As indicated above, many of the alpha groups which are virtually unhindered have been classified as "favored" and are thought to be cases in which the initial and final wave functions of the odd nucleon are nearly the same. The odd-nucleon alpha emitters apparently always have at least one such favored mode of decay for which the hindrance factor is as low as one or two and seldom exceeds five; for the even-odd emitters such favored decays almost always include a group not too far from the ground-state transition energy (less than 0.3 Mev). Among the isotopes of neutron number greater than 138, a parity change in alpha decay is often accompanied by a large (greater than 100) hindrance factor. (It should be recalled that all cases of odd angular momentum carried off by the alpha particle correspond to parity change.) The data on hindrance factors for the alpha decay of odd-odd nuclei is, unfortunately, too meager to allow any generalizations.

There seems to be some regularity in the hindrance of the alpha decay of even-even emitters. The decay to the ground state is essentially unhindered, and the decay to the 2+ state is hindered only by a factor of one to four, while the decay to the 4+ state has F equal to about ten up to a thousand. The decay to the 6+ state has F generally equal to several hundred, while the decay to the 8+ state has F equal to several thousand. The alpha groups carry away angular momentum 0, 2, 4, 6, 8, etc. These empirical hindrance factors are taken as the standards for the effect of angular momentum on the alpha decay of nearby odd-A nuclides as mentioned above. Although only the hindrances corresponding to even angular momenta are given, these are all that are needed in considerations of favored decay, which involves no parity change. The above-mentioned vector-coupling coefficients are unity for even-even nuclides. For any given nucleus the hindrance factors may be related to an alpha probability distribution on the spheroidal nu-

clear surface, as has been shown by Rasmussen and B. Segall and by P. O. Fröman. It is essential for solution of the wave equation to take into account the interaction of the outgoing alpha waves with the quadrupole field of the nucleus. The striking trends of hindrance factors with atomic number may be related to a shift in alpha probability at the nuclear surface from the poles toward the equator.

It has not been possible in this short treatment of alpha decay to describe many of the extensions beyond the simple one body theory that have been in the process of development over a period of years. These include detailed considerations of the potential in which the alpha particle finds itself in the nuclear interior, how the components of the alpha particle are assembled, the effect of many daughter states on the alpha decay to a given state, etc. As early as 1937 H. A. Bethe made considerations concerning the formation of the alpha particle in the decay process for the many body model. T. Sexl and M. A. Preston have made careful derivations of the decay rate probability; Preston has studied the effect of spin change on the frequency and barrier penetration factors. J. J. Devaney, Rasmussen, and others have considered the effect of level spacing in the daughter nucleus. G. H. Winslow and O. C. Simpson have made many improvements in the one-body treatment and have investigated the effect of the potential of the alpha particle in the nucleus in some detail. H. A. Tolhoek and P. J. Brussard have presented a fresh approach to alpha-decay-rate theory, using a very strong attractive nuclear potential for the alpha particle and a nucleon overlap approach to the problem of alpha particle formation.

3.6 Gamma Transition Rates

For those heavy nuclei in the region of spheroidal deformation (roughly $N > 138$) there has come in recent years a great increase in knowledge of gamma transition properties. Nuclear gamma transitions can be conveniently classified according to multipolarity. Except in special cases, a transition will proceed by the lowest multipolarity, since the lifetimes of competing higher multipoles will generally be much slower as a consequence of the fact that the

gamma-ray wave lengths are much greater than nuclear dimensions.

By way of review, let us set down the strict selection rules for gamma transitions, selection rules in the good quantum numbers, I, the total nuclear angular momentum, and π, the parity. Radiation of multipolarity L carries off an angular momentum of $L\hbar$; hence, it follows from conservation of angular momentum that the allowed L values comprise the integers ranging between the difference and the sum of the initial and final spins.

$$|I_i - I_f| \leq L \leq |I_i + I_f|.$$

Electric multipole radiation has the associated parity $(-1)^L$, while magnetic multipole radiation has parity $(-1)^{L+1}$. Conservation of parity imposes an additional restriction, and the complete strict selection rules are implicit in Table 3.5, where the letter E means electric and M means magnetic radiation.

TABLE 3.5 *Standard Notation of Gamma Transitions*

L	0	1	2	3	4	5
NAME	MONOPOLE	DIPOLE	QUADRUPOLE	OCTUPOLE	2^4-POLE	2^5-POLE
No parity charge	*	$M1$	$E2$	$M3$	$E4$	$M5$
Parity charge		$E1$	$M2$	$E3$	$M4$	$E5$

* A radiative (1 photon) transition is not allowed for $L = 0$, but the $E0$ transition may occur by pure internal conversion of penetrating electrons ($s_{1/2}$ or $p_{1/2}$).

The most powerful experimental method for establishing gamma multipolarities is the determination of conversion coefficients and comparison with theoretical values. Another general method involves angular correlation studies.

Gamma lifetimes (emission partial lifetimes) are often compared with some form of the so-called single-proton formula. Measured lifetimes for most multipolarities agree only moderately well with those calculated from the formula. The transitions best obeying the formula are the $M4$ isomeric transitions whose measured lifetimes agree well with the formula except that the decay is one order of magnitude slower than the calculated rate. The Moszkowski form of the single-proton expression is given in Table 3.6. In these for-

TABLE 3.6 *Moszkowski Single Proton Gamma-Transition Rate Formulae*

MULTIPOLARITY	RATE CONSTANT, $1/\tau$ (IN SEC^{-1})
$E1$	$1.5 \times 10^{14} A^{2/3} E_\gamma^3 S$
$M1$	$2.8 \times 10^{13} E_\gamma^3 S$
$E2$	$1.6 \times 10^{8} A^{4/3} E_\gamma^5 S$
$M2$	$1.2 \times 10^{8} A^{2/3} E_\gamma^5 S$
$E3$	$1.1 \times 10^{2} A^{2} E_\gamma^7 S$
$M3$	$1.8 \times 10^{2} A^{4/3} E_\gamma^7 S$
$E4$	$5.0 \times 10^{-5} A^{8/3} E_\gamma^9 S$
$M4$	$1.5 \times 10^{-4} A^{2} E_\gamma^9 S$
$E5$	$1.6 \times 10^{-11} A^{10/3} E_\gamma^{11} S$
$M5$	$7.5 \times 10^{-11} A^{8/3} E_\gamma^{11} S$

mulae E_γ is the transition energy in Mev, A the mass number, and S a statistical factor dependent on the initial and final spins and l values, and on the multipolarity of the transition. The factor S is often assumed to be unity for purposes of comparisons of the calculated with the experimental values.

In another method of comparison of gamma lifetimes the so-called reduced transition probability, a quantity proportional simply to the nuclear matrix element squared, is calculated. A relevant formula, given by A. Bohr and Mottelson, for both electric and magnetic multipoles is:

$$\frac{1}{\tau} = \frac{8\pi(L+1)}{L[(2L+1)!!]^2} \frac{1}{\hbar} \left(\frac{E}{\hbar c}\right)^{2L+1} B_L$$

where E is the gamma energy, c is the speed of light, τ is the mean life in seconds, and B_L is the reduced transition probability.

The unified model, as mentioned above, introduces selection rules involving the auxiliary quantum numbers. Of especial importance is the selection rule involving the quantum number, K, which states that the multipolarity of the transition must equal or exceed the change in K (i.e. $L \geq \Delta K$). The weaker selection rules in the asymptotic quantum numbers N, n_z, Λ and Σ will be discussed later and are summarized in Table 3.7.

3.6a Transitions in Even-Even Nuclei

The even-even nuclei in the region of spheroidal distortion exhibit several general spectral features. As mentioned earlier, based on the 0+ ground state is a closely spaced (~42-100 Kev

first excited states) rotational band with the 2+, 4+, 6+, 8+, etc. level sequence. The gamma transitions connecting these rotational states are pure $E2$ transitions. The reduced transition probabilities between the ground and the first excited state have been determined from Coulomb excitation experiments for U^{238} and Th^{232}, and they are one to two orders of magnitude faster than those estimated from the single proton formula. Application of the Copenhagen model leads to the explanation of these fast rates as resulting from a rotational transition of the deformed nucleus, which for a large intrinsic quadrupole moment Q_0, is equivalent to the cooperative motion of many nucleons.

The next rotational band often found above ground in the heavy even-even nuclei is a band with a 1− base state (possibly octupole vibrational states, see Section 3.8a). The 1− state decays to the ground (0+) and first excited (2+) states by electric dipole transitions. The reduced transition probability to the first excited state in the numerous cases studied is about twice that to the ground state. The unified model formalism of G. Alaga, K. Alder, Bohr, and Mottelson treats such ratios of reduced transition rates to two or more states of a common rotational band as simply involving geometrical considerations of vector addition. The ratios should be functions of the multipolarity, the nuclear spins, and the associated K quantum number of the initial and final states. (To the extent that K is not an absolutely good quantum number, the theoretical ratios may be inexact.) The experimental ratios for transition from 1− states yield the important result that the K quantum number of the lowest 1− state is zero. A recent theoretical formulation of Bohr and Mottelson relates the absolute $E1$ transition rates to a product of quadrupole and average octupole surface deformation. They apply the theory to $E1$ lifetime information in Sm^{152} and Th^{228}.

In the vicinity of just below 1 Mev there have been encountered in several even-even nuclei by Asaro and Perlman a 0+ state, which has the "earmarks" of the first excited, beta vibrational level (retention of spheroidal symmetry) predicted by Bohr and Mottelson. This state in the few well-studied cases decays to the ground state by pure electric monopole radiationless internal conversion at a rate roughly comparable to its decay by $E2$ radiation to the first

excited state. There is indirect evidence from Coulomb excitation in Th^{232} by P. H. Stelson and F. K. McGowan that the $E2$ transitions connecting this beta vibrational band to the ground band occur at rates slightly in excess of those calculated by the single proton formula. Such evidence supports the idea that these levels indeed have collective vibrational character.

Slightly above the beta vibrational band there has been found in several cases a band with spin sequence 2+, 3+, etc. This 2+ state decays characteristically by $E2$ radiation to the 0+, 2+, and 4+ states of the ground band, although the decay to the 4+ state is weak. The vector addition relations neatly explain the relative gamma intensity pattern if this 2+ state is assigned a K quantum number of 2. The lack of detectable $M1$ radiation in the $2+ \rightarrow 2+$ transition to the first excited state may be attributed to operation of the approximate K selection rule, that the multipolarity L must be greater than or equal to the change in K, $|K_i - K_f|$. This $K = 2$ band may be associated with the predicted gamma vibrational band (i.e. the vibrational motion characterized by change in spheroidal symmetry). There is no experimental measurement yet giving the lifetime of any states of a gamma vibrational band.

3.6b Transitions in Odd-Mass Nuclei

The greater level density of the odd-mass nuclei over even-even nuclei makes for greater experimental difficulties, and a greater diversity of gamma transition types.

As in even-even nuclei, we find rotational bands, but with spin sequences I_0, $I_0 + 1$, $I_0 + 2$, etc. The characteristic intra-band radiation pattern involves fast pure $E2$ transitions connecting alternate levels and $M1$-$E2$ mixed transitions connecting adjacent levels. Some of the $E2$ transition probabilities have been measured by J. O. Newton by Coulomb excitation in U^{233}, U^{235}, Np^{237}, and Pu^{239} and have been found to be of the fast, rotational type. The $M1$ transitions are of rates comparable to estimates made with the single-particle formula, and they are related in the Bohr-Mottelson formalism to static magnetic properties of the rotational states.

For interpretation of the radiations connecting different rotational bands the K selection rules and additional weaker selection

rules in the other approximate quantum numbers have proved most useful. It is difficult to make generalizations in this particular area, since a large variety of considerations arise in particular cases. Examples of approaches in interpretation of interband radiations in odd-A nuclei have been provided by J. M. Hollander, W. G. Smith and J. W. Mihelich (in Pu^{239}), Hollander, Smith, and Rasmussen (in Np^{237}), and Rasmussen, F. L. Canavan, and Hollander (in Np^{237}). As in even-even nuclei, the odd nuclei provide numerous examples of the validity of the K selection rules.

An interesting class of inter-rotational-band transitions is that of the numerous low-energy $E1$ transitions. Many of them have measured lifetimes and are retarded from the single proton estimate by factors of 10^4-10^6 (cf. Fig. 3.17) even though they do not violate the K-selection rules. Examples of even greater retardation are known for K-forbidden $E1$ transitions—as, for example, in Pu^{239}.

The extraordinary slowness of the low-energy $E1$ transitions as discussed by D. Strominger and Rasmussen has been associated with the fact that all of them violate approximate selection rules which are strict in the limits of no spheroidal deformation and of very large spheroidal deformation. The approximate selection rules in the spherical limit will be rules involving l and j, the odd-nucleon orbital angular momentum and total angular momentum, respectively. For $E1$ transitions the only allowed cases are $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$, and the j selection rule would be violated for $E1$ transitions within a major shell. Of greater utility for deformed nuclei are the selection rules in the large deformation limit. As this limit is approached, the asymptotic quantum numbers N, n_z, Λ, and Σ discussed previously will signify properties of the odd-nucleon wave function which are nearly constants of the motion. These quantum numbers are given beside the various orbitals in Nilsson's energy level diagrams (Figs. 3.14 and 3.15). The selection rules for dipole and quadrupole radiation are given in Table 3.7 as derived by R. R. Chasman and Rasmussen. If the combination of asymptotic quantum number changes between the initial and final states is not found in Table 3.7, then the transition rate is expected to be retarded. Similar selection rules have been derived and applied by Mottelson and Nilsson and by G. Alaga.

A curious phenomenon, only partially understood theoretically,

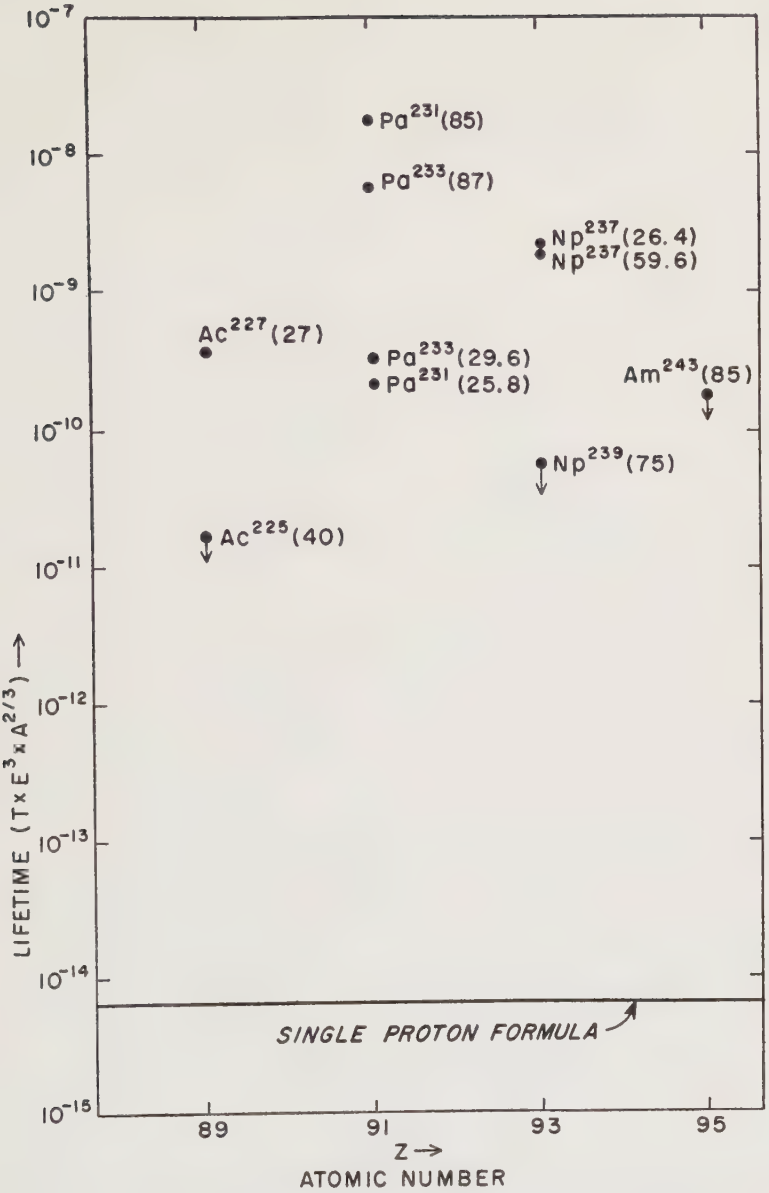


Fig. 3.17 Experimental $E1$ transition lifetimes in the actinide region. (The energy of the transition, in Kev, is given in parentheses.)

TABLE 3.7 *Changes in Asymptotic Quantum Numbers Favoring Gamma Transitions (asymptotic selection rules)*

	ΔN	Δn_z	$\Delta\Lambda$	$\Delta\Sigma$
$E1$	$+1$	$+1$	0	0
	-1	-1	0	0
	± 1	0	± 1	0
$E2$	$+2$	$+2$	0	0
	-2	-2	0	0
	0, ± 2	0	0	0
	0, ± 2	± 1	± 1	0
	± 2	0	± 2	0

	ΔN	Δn_z	$\Delta\Lambda$	$\Delta\Sigma$
$M1$	0	0	0	± 1
	0, ± 2	± 1	± 1	0
	0, ± 2	0	0	0
$M2$	± 1, ± 3	± 1	0, ± 2	0
	± 1, ± 3	0	± 1	0
	± 1, ± 3	± 2	± 1	0
	± 1	0	± 1	± 1
	± 1	± 1	0	± 1

is that some of the slowest $E1$ transitions (e.g. 85 Kev in Pa^{231}, 59 Kev in Np^{237}) exhibit anomalously large internal conversion coefficients. L_I and L_{II} subshell conversion seems most susceptible, while L_{III} conversion is usually quite normal. The anomalies probably arise from the fact that the electron orbitals in question penetrate inside the nuclear volume.

Less is known in a systematic way about lifetimes for interband radiation when we come to consider multipolarities other than $E1$.

Slow $M1$ transitions from the 286-Kev state to the ground band occur in Pu^{239}. The retardation is attributable to violation of the K-selection rule ($\Delta K = 2$ in this case). The $E2$ radiation from the same state also appears to be somewhat retarded and this may be attributed to violation of a selection rule in Σ ($\Delta\Sigma = -1$ in this case, with no change in Σ allowed for any electric transition). There occurs in Np^{237} a 208-Kev $M1$ transition which is highly retarded, and a 164-Kev $E2$ transition which is also quite retarded. The retardation has been attributed to violation of selection rules in n_z, Λ, or Σ according to Rasmussen, Canavan, and Hollander.

Very little is known concerning $M2$ transitions in the heavy region. An $M2$ transition of measured rate and 234-Kev energy is known in Np^{237}. Its rate is only about two orders of magnitude below the single particle lifetime estimate. It is allowed by the K and the asymptotic quantum number (N, n_z, Λ) selection rules.

An interesting $E3$ isomer has recently been discovered lying about 0.07 Kev above ground in U^{235} by F. Asaro and I. Perlman, and J. R. Huizenga, C. L. Rao, and D. W. Engelkemeir. It exhibits a half life of 27 minutes, and is this short-lived by virtue of

an enormous ($>10^{21}$) conversion coefficient. The transition is allowed by K selection rules but violates the selection rule in n_z and Λ. The partial lifetime for photon emission is somewhat too uncertain to make possible a comparison with an estimate from the single proton formula.

3.7 Beta-Decay Rates

The classification and understanding of beta transitions of the heavy elements has lagged behind classification of gamma and alpha transitions because of experimental difficulties. The common methods of resolving Fermi-Kurie plots of the beta spectra are usually inadequate where possible final states are as close-lying as they are throughout the heavy region. Levels of both parities are widely interspersed in the odd-A nuclei as evidenced by the prevalence of low-energy $E1$ gamma transitions. The neutron deficient isotopes decay by electron capture with negligible positron branching and thus offer no direct measure of their decay energies. Coincidence measurements and the differences of gamma transition intensities for transitions leaving and proceeding to a given level provide indirect means of determining beta and electron-capture branching to various final states.

The wide prevalence of alpha decay has made possible rather extensive calculation and estimation of total electron capture and beta-decay energies (cf. Section 3.2).

In beta decay there is a transformation of a neutron into a proton with the creation of a negative electron and an antineutrino. The spectacular recent predictions and discoveries that parity is not conserved in beta decay have reopened the field to intense theoretical and experimental activity. At present writing it appears that of the five possible relativistically invariant interactions in beta decay, the polar vector (V) and axial vector (A) interactions are, in fact, applicable. The former is a Fermi type interaction with the beta particle and the neutrino having antiparallel spins, and the latter is a Gamow-Teller type interaction with the beta particle and the neutrino having parallel spins. The new knowledge for the most part should not invalidate the earlier approaches to classification of beta decay according to spin and

parity selection rules. If the $\beta - \bar{\nu}$ pair is emitted with no net orbital angular momentum, the beta decay is classed as allowed, regardless of its rate; there must be no parity change between initial and final nuclear states, and $\Delta I = 0, \pm 1$. If the $\beta^- - \bar{\nu}$ pair is emitted with one unit of net orbital angular momentum, the decay is classed as first-forbidden; there must be a parity change, and $\Delta I = 0, \pm 1, \pm 2$.

In the past, correlations of ft values (which measure the nuclear matrix elements) for lighter nuclei have found considerable success in grouping allowed beta decay in the log ft range 4.0–5.5 (the superallowed mirror transitions being exceptions with ft values near 3.2) and first-forbidden in the range log ft 6.0–8.5. R. W. King and D. C. Peaslee further found evidence for grouping within the first forbidden classification, $\Delta I = 0$ corresponding to log ft around 6.5, $\Delta I = 1$ corresponding to log ft around 7.5, and $\Delta I = 2$ corresponding to log $f_1 t$ about 8.5 (where f_1 is a special f function appropriate to the case $\Delta I = 2$, yes, and approximately equal to $\frac{(W^2 - 1)}{20} f$, with W the relativistic energy equal to $1 + \frac{E_{max}}{mc^2}$). In the course of time many exceptions to the ft groupings have been found, such as very slow allowed transitions and some fast (log $ft = 5$) first forbidden transitions near the closed-shell nuclide Pb^{208}.

Allowed and first forbidden, $\Delta I = 0, \pm 1$, transitions are usually not distinguishable by beta spectrum shape determinations (Bi^{210} is a notable exception). The $\Delta I = 2$, yes, or so-called Gamow-Teller unique first-forbidden transitions, do exhibit a definite spectral shape which is different from the allowed shape. There is, perhaps, one case of such a spectral shape in the actinide region. S. A. Baranov and K. N. Shlyagin resolved a plot of the close-lying beta groups of the 16-hour Am^{242m} and believe the beta spectrum to the first excited (2+) state shows the shape characteristic of the $\Delta I = 2$, yes, transition.

The beta-decay energies, group intensities, half lives and log ft values (calculated from graphs of E. Feenberg and G. L. Trigg) are given in Table 3.8 for some even-A isotopes. The case of Np^{238} has been the subject of considerable earlier analysis and study. There has been no clear assignment of parity to Np^{238}, but the spin

TABLE 3.8 *Beta-Decay ft Values and Classifications in Even-A Nuclei*

ISOTOPE	BETA ENERGY (Kev)	HALF LIFE	GROUP INTENSITY (%)	LOG *ft*	STATE ASSIGNMENTS INITIAL *I*, π, *K*	STATE ASSIGNMENTS FINAL *I*, π, *K*	CLASSIFICATION (FORBIDDENNESS)
Ac^{228}	2180	6.13 h	10	8.9			
	1850		9.6	8.6			
	1700		6.7	8.7			
	1110		53	7.1			
	640		7.6	7.0			
	450		13	6.3			
Pa^{234}(UZ)	1130	6.66 h	13	7.8			
	530		27	6.4			
	320		32	5.6			
	160		28	4.7			
$Pa^{234m}(UX_2)$	2310	1.175 m	90	5.6			
	1500		9	5.9			
	580		1	5.4			
Np^{238}	1240	2.10 d	45	8.3	2, $\pm$, 2	2, +, 0	All. or 1st—K forb.
	1130		2	9.5		4, +, 0	All. or 1st—K forb.
	290?		7	7.0		?	
	250		**39**	**6.1**		2, +, 2	All. or 1st.
	200		7	6.5		3, +, 2	All. or 1st.
Np^{240m}	2.156	7.3 m	52	6.5		0, +, 0	
	1.59		31	6.3			
	1.26		11	6.3			
	0.76		5.4	5.9			
U^{240}	0.36	14.1 h	100	5.6	0, +, 0		
Am^{242m}	620	16.01 h	40	6.9	0, −, 0?*	0, +, 0	1st
	578		41	6.7		2, +, 0	1st (unique)

* Assignment is by S. A. Baranov and K. N. Shlyagin, who claim that 578-Kev group exhibits $\Delta I = 2$, yes, spectral shape.

has been determined as two from atomic beam measurements by J. C. Hubbs, R. Marrus, and R. G. Albridge. The important conclusion to be drawn from the Np^{238} beta decay is that the K selection rules can be very restrictive. Violation of the K selection rule that the multipolarity ($L = 0$ or 1 for allowed, $L = 0$, 1 or 2 for first forbidden) must equal or exceed the change in K has resulted in over two orders of magnitude retardation for the energetic beta group which decays from the level with designation $2\pm$ and $K = 2$ to the level at 44 Kev with the designation $2+$ and $K = 0$, compared to the decay to the high-lying level of designation $2+$ with $K = 2$ (see the 1240- and 250-Kev beta groups in Table 3.8).

In Table 3.9 the analogous beta-decay information for some odd-mass isotopes is given. The K selection rules would be expected to be quite restrictive here, too, but we have no certain examples in such odd-A nuclei. Of greatest promise in classifying beta decay of odd-A spheroidal nuclei are the selection rules in the asymptotic quantum numbers (N,n_z,Λ). Alaga has given and applied these selection rules to deformed nuclei in the rare earth region and has shown that violation of selection rules in these quantum numbers results on the average in one order of magnitude retardation. In Table 3.9 we retain his notation u for "unhindered" and h for "hindered," referring to these special selection rules. G. Alaga's selection rules may be given in abbreviated form for a Gamow-Teller interaction as shown in Table 3.10.

Of the fourteen entries in Table 3.9 for which quantum state assignments are proposed, the log ft values for eleven cases fall in a relatively narrow range between 5.7 and 7.0. In this group there are six cases classified first forbidden, unhindered, four cases classified allowed, hindered, and one which may be either of the two above classifications. There is one case with log $ft = 9.2$ and one with the limit log $ft > 9.0$, with the classifications first forbidden, hindered. There is one case of an unobserved group, classified allowed, hindered, in which the limit log $ft > 8$ could be set and which thus falls outside the usual range for this classification; Hollander has suggested that the violation in this case of the selection rule in N, which occurs in addition to the violation of the selection rule in n_z, has special importance.

TABLE 3.9 *Beta-Decay ft Values and Classifications in Odd-A Nuclei*

ISOTOPE	BETA ENERGY (Kev)	HALF LIFE	GROUP INTENSITY (%)	LOG *ft*	STATE ASSIGNMENTS INITIAL $I\pi, K(N n_z \Lambda)$	STATE ASSIGNMENTS FINAL $I\pi, K(N n_z \Lambda)$	CLASSIFICATION (FORBIDDENNESS)
Ac^{227}	45.5	22 y	100	6.8	3/2−, 1/2(530)?	1/2−, 1/2(501)?	All. *h*
Th^{231}	(384)	25.6 h	<0.1	>9.0	5/2+, 5/2(633)?	3/2−, 3/2(521)	1st *h*
	299		38	5.9		5/2+, 5/2(642)	All. *h*
	218		33	5.6			
	134		20	5.1			
	90		8	5.0			
Pa^{233}	568	27.4 d	5	9.2	3/2−, 3/2(521)	5/2+, 5/2(633)	1st *h*
	257		58	7.0		3/2+, 3/2(631)	1st *u*
	145		37	6.4		1/2+, 1/2(631)	1st *u*
U^{237}	248	6.75 d	95	6.1	1/2−, 1/2(501)?	3/2−, 3/2(521)	All. *h*
Pu^{241}	20.5	13.0 y	100	5.7	5/2+, 5/2(622)	5/2−, 5/2(523)	1st *u*
Pu^{243}	566	4.98 h	53	6.1	7/2+, 7/2(624)? or	5/2−, 5/2(523)	1st *u*
	468		35	6.0	5/2+, 5/2(622)	5/2+, 5/2(642)	All. *h*
Am^{239} (E.C.)	506	12 h	~82	~5.9	5/2−, 5/2(523)	5/2+, 5/2(633)	1st *u*
	388		<2	>8		7/2−, 7/2(743)	All. *h*
	268		~17	~6.0		5/2+, 5/2(622)	1st *u*
Bk^{249}	80	290 d	100	6.3	7/2+, 7/2(633)	7/2+, 7/2(624) or 9/2−, 9/2(734)	All. *h* or 1st *u*

TABLE 3.10 *Beta-Decay Selection Rules*

	STRICT SELECTION RULES		APPROXIMATE SELECTION RULES			
CLASSIFICATION	I	*Parity Change*	ΔK	ΔN	Δn_z	$\Delta\Lambda$
Allowed	0, ±1	no	0, ±1	0	0	0
First forbidden*	0, ±1	yes	0, ±1	±1	0	±1
(nonunique)					±1	0
First forbidden	±2	yes	0, ±1, ±2	±1	0	±1
(unique)					±1	0

* In the nonunique case there are several beta-decay matrix elements to be considered, and Alaga gives selection rules separately for them. The meaning of the entries in this table is that unless one of these selection rules is violated, there will be at least one important matrix element contributing.

The occurrence of allowed, unhindered, transitions in odd-A nuclei of the actinide region seems highly unlikely from inspection of the Nilsson level diagrams (Figs. 3.14 and 3.15) and consideration of the corresponding levels into which proton and neutron filling is proceeding.

On the basis of the small number of actinide beta-decay groups that can presently be classified with confidence, it is quite clear that an ft value alone will usually be insufficient to allow classification of a transition as allowed or first forbidden and hence insufficient to permit conclusions about parity changes in beta decay. Selection rules in the various auxiliary quantum numbers, especially K and N, but also n_z, Λ, and Σ, have important influence on beta-decay rates.

We have seen in Table 3.9 that no odd-A isotope is without at least one beta-decay group in the abundant class of allowed h, or first forbidden u (log ft 5.7–7.0) and that none exhibits any beta group with log $ft < 5$.

3.8 Energy Levels and Illustrative Decay Schemes

A number of data on energy levels and a number of decay schemes will now be considered in the light of the Bohr unified model. Such information is gained from experimental determination of ground-state spins by various methods, from study of alpha and beta decay, and by determination of the multipolarity of

gamma transitions. Additional information on the details of nuclear states is given by nuclear magnetic moments, by measurement of angular correlation of nuclear radiations and of Coulombic excitations, and by the study of energy level patterns.

First we shall use the Nilsson diagrams given above in Figs. 3.14 (for neutrons) and 3.15 (for protons) to determine the probable theoretical orbital assignments, and hence the probable theoretical nuclear spins and parities for a number of ground- and low-lying states for odd-A nuclei and shall compare these with measured values where possible. These orbital assignments are determined in the following way. If one knows the deformation, δ, of the nucleus, one merely moves out to the abscissa corresponding to this deformation and then moves vertically through the diagram, counting each state twice (each state is doubly degenerate corresponding to the two possible signs of Ω) until the state corresponding to the last particle is reached. This state should then correspond to the observed ground state in spin and parity. If one or more of the Nilsson state lines happen to be quite close together, it may be that the ground state will actually correspond to one of the other states

TABLE 3.11 *Odd Neutron Ground State Spin Assignments*

NUCLIDE	SPIN, I	NILSSON ORBITAL $\Omega\pi$, $[N\, n_z\, \Lambda]$	NEUTRON NUMBER
U^{233}	5/2	5/2+, [633]	141
U^{235}	7/2	7/2−, [743]	143
Pu^{237}	(7/2)	7/2−, [743]	
U^{237}	1/2	1/2+, [631]	
Pu^{239}	1/2	1/2+, [631]	145
Cm^{241}	(1/2)	1/2+, [631]	
U^{239}	(5/2)	5/2+, [622]	
Pu^{241}	5/2	5/2+, [622]	147
Cm^{243}	5/2	5/2+, [622]	
Pu^{243}	(7/2)	7/2+, [624]	
Cm^{245}	7/2	7/2+, [624]	149
Cf^{247}	(7/2)	7/2+, [624]	
Cf^{249}	9/2	9/2−, [734]	151

(underlined spins are measured, while others come from decay scheme data with uncertain values in parentheses)

because of the approximations in the treatment. In the case of such states lying close together, all should be observed among the low-lying levels of the nucleus. The specific orbital chosen for the last odd particle depends on an enlightened choice of the deformation parameter.

Table 3.11 lists the ground-state spins and suggested Nilsson level assignments for the odd neutron nuclei of uranium and heavier elements. The quantum number Ω corresponds in these cases to the nuclear spins (total nuclear angular momentum, I). Below uranium the situation does not seem to be so well defined, possibly because the strong coupling approximations are becoming less valid. It can be seen that the agreement between the measured spins and the theoretical values of Ω is excellent. Table 3.12 gives the

TABLE 3.12 *Odd Neutron Excited State Spin Assignments with Energies in Kev*

	NILSSON ORBITAL $\Omega\pi$, $[N\ n_z\ \Lambda]$				
NUCLIDE	7/2−, [743]	1/2+, [613]	5/2+, [622]	7/2+, [624]	9/2−, [734]
U^{235}	0	<0.1			
Pu^{237}	(0)	145			
U^{237}		(0)	145		
Pu^{239}	392	0	286	512	
Cm^{241}		(0)			
U^{239}			(0)		
Pu^{241}			0	172	
Cm^{243}			0		
Pu^{243}				(0)	
Cm^{245}		(631)	252	0	394
Cf^{247}				(0)	
Cf^{249}					0

(lack of notation indicates spins for which there is strong experimental evidence; parentheses indicate spins for which there is slight experimental evidence; nuclides for which there are no decay scheme data have not been included)

energy in Kev at which the Nilsson levels occur in various nuclei of uranium and heavier elements with an attempted correlation with excited as well as ground states. These data are, for the most part, tentative. Table 3.13 lists the ground-state spins and suggested level assignments for odd proton nuclei, where the situation

TABLE 3.13 *Odd Proton Ground State Spin Assignments*

NUCLIDE	SPIN, I	NILSSON ORBITAL $\Omega\pi$, $[N\ n_z\ \Lambda]$
$_{91}Pa^{231}$	3/2	3/2−, [521]
$_{93}Np^{237}$	5/2	5/2+, [642]
$_{93}Np^{237m}$	—	5/2−, [523]
$_{93}Np^{239}$	5/2	5/2+, [642]
$_{95}Am^{241}$	5/2	5/2−, [523]
$_{95}Am^{243}$	5/2	5/2−, [523]

(indicated spins are measured values)

is not so satisfactory for the excited states. This may be due, in part, to the reversal of the $f_{7/2}$ and $h_{9/2}$ orbitals in Nilsson's calculations. The 9/2 spin of Bi^{209} would seem to indicate that $h_{9/2}$ should be below $f_{7/2}$.

3.8a Even-Even Nuclei

Next we present for purposes of illustration in Fig. 3.18 an idealized energy level scheme for a heavy even-even nuclide in the region of strong deformation, where the unified model may be expected to be applicable. This hypothetical nucleus has a well-developed rotational band based on the ground state and has

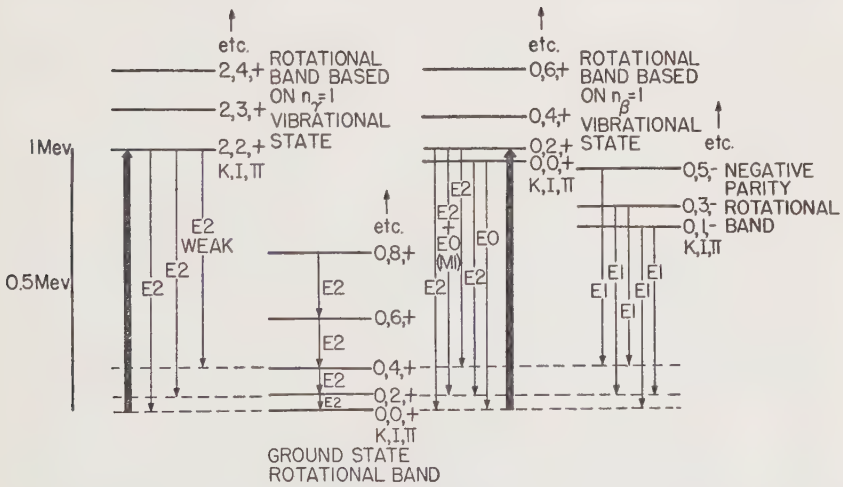


Fig. 3.18 Pattern of rotational and vibrational levels for an idealized even-even nucleus in the region of deformed nuclei. The expected gamma-ray pattern is also shown.

rotational bands at about one Mev of excitation energy based on the first beta vibrational state (characterized by retention of spheroidal symmetry) and the first gamma vibrational state (characterized by loss of spheroidal symmetry). The energy spacing of the rotational levels is proportional to $I(I+1)$ as the theory suggests it should be (see below). The three quantum numbers K (component of total angular momentum along the symmetry axis), I (the total angular momentum or spin), and π (the parity) are designated for each of the states in these three rotational bands. Some $E2$ and $E0$ gamma ray transitions which should be strong (or weak) according to simple vector addition considerations involving the spins and K quantum numbers are indicated, and, similarly, some inverse transitions which should be strongly excited by Coulombic excitation are designated. A negative-parity rotational band, which is less well understood, is also included, a matter which is discussed below; here the expected $E1$ gamma transitions are indicated.

An examination of the decay schemes of the even-even isotopes of thorium, uranium, plutonium, curium, californium, and fermium (see Table 3.14) reveals a common pattern and evidence for rotational bands. The sequence of levels in the daughter nucleus reached by alpha decay has the spin and parity designations, 0+ (ground), 2+, 4+, 6+, and 8+, and the position of these levels above ground is approximately 45, 150, 300, and 500 Kev, respectively, for the cases where they have all been found. De-excitation of these levels occurs by a cascade of $E2$ gamma transitions with no crossover transitions. The expected electric-quadrupole nature of these transitions has been characterized by measurement of absolute conversion coefficients, relative L subshell conversion coefficients, and alpha-gamma angular correlations. The regularity of the pattern is evident from Table 3.14.

As stated above (in Section 3.4), the unified model predicts a rotational band of levels in which even states (0+, 2+, 4+, . . .) appear for an even-even nucleus. The energy spacing of such levels should be proportional to $\frac{\hbar^2}{2\mathfrak{I}}[I(I+1)]$ where $\frac{\hbar^2}{2\mathfrak{I}}$ is the rotational unit of energy, and I is the total angular momentum (nuclear spin) of the state. This spacing agrees closely with the experimental

TABLE 3.14 *Energy in Kev of Excited Levels in Daughter Nucleus of Indicated Even-Even Alpha Emitters*

	ENERGY OF LEVELS				
NUCLEUS	2+	4+	6+	8+	$\frac{\hbar^2}{2\mathfrak{I}}$
Ra^{222}	112	309			18.67
Ra^{224}	84.47	253			14.08
Ra^{226}	67.62	210	416		11.27
Ra^{228}	59				
Th^{226}	72.13	226.4			12.02
Th^{228}	57.5	186.1			9.58
Th^{230}	53	173			8.73
Th^{232}	50	163			8.33
Th^{234}	48				8.00
U^{230}	51.7				7.83
U^{232}	47.5	156	321		7.917
U^{234}	43.50	143.31	296.4	499	7.25
U^{236}	44.2				
U^{238}	45				7.50
Pu^{236}	43.4				
Pu^{238}	44.11	146.0	303.7	514	7.37
Pu^{240}	42.88	141.8	292		7.16
Pu^{242}	44.6				
Cm^{242}	42.12	140	291		7.02
Cm^{246}	42.9	140			7.15
Cm^{248}	43.4	143			7.23
Cf^{250}	42	139			7.00

values given in Table 3.14, which shows a value of $\frac{\hbar^2}{2\mathfrak{I}}$ approaching 7.5 to 7.0 Kev for the higher mass nuclides. A detailed comparison of the data with the predictions of the unified model makes it appear highly likely that the excited levels observed in alpha decay of even-even nuclei correspond to such bands of rotational levels. It will be noticed that at the lower end of this region the value of $\frac{\hbar^2}{2\mathfrak{I}}$ becomes larger, i.e. the energy position of the 2+ level is higher. In general, with decreasing neutron number this trend continues, gradually leading to the properties in the transition region—that is, the region where the nucleus is soft toward collective vibrations.

Odd-parity excited states, mentioned in Section 3.6a, have been

observed in the alpha decay of some even-even isotopes in addition to the even states. In the case of Th^{228} decay, the well-characterized $1-$ level appears only 217 Kev above the ground state of the Ra^{224} daughter. This may be the lowest state of an odd spin and parity rotational band with associated $3-$ and $5-$ levels at 289 and 412 Kev, respectively. Similarly in the decay of ionium, Th^{230}, a rotational band of negative parity with levels $1-$ (253 Kev), $3-$ (320 Kev), and $5-$ (445 Kev) is observed in addition to a $2+$, $4+$, $6+$ level sequence at 68, 210, and 416 Kev, respectively. Such odd-parity states have been looked for in the transuranium-element region, but only in the cases of Pu^{238} and Pu^{240} has evidence for such a state appeared. In Cm^{242} alpha decay, the assignment, $1-$, is given to a level at 605 Kev which is populated by alpha decay only to the extent 3×10^{-6}. Other high-lying odd-parity states probably exist in the transuranium-element region, but because of their location high above the ground state, they are reached in only an extremely small percentage of the alpha transitions and hence are extremely difficult to investigate.

The current interpretation is that these negative parity states represent octupole vibrational states based on the $0+$ intrinsic ground states of these heavy even-even nuclei. R. F. Christy, for example, has suggested that such states could arise for nuclear deformations into a pear shape. Theoretical treatments by the Copenhagen theoretical group based on octupole mode of vibrations offer a promising approach to this interesting problem.

Concerning the expected first beta- and gamma-vibrational (quadrupole vibrations) excited states there is increasing evidence that they occur at around one Mev in transuranium nuclides. Such states were discussed earlier in the section on gamma transitions (Section 3.6a).

The nucleus Pu^{238} is one whose level scheme has been well studied and has features approximating those shown for the idealized case shown in Fig. 3.18 above. Thus the level scheme of this nucleus can serve as an excellent illustrative example, and it is, therefore, pictured in some detail in Fig. 3.19. This figure shows the alpha-decay scheme of Cm^{242}, the beta-decay scheme of Np^{238}, and the preliminary electron capture decay scheme of Am^{238} to the common daughter nucleus Pu^{238}. The vertical arrows representing

the experimentally observed gamma transitions indicate qualitatively by their width the relative transition intensities. Spin and parity assignments are given on the left-hand side of a level, those in parentheses being somewhat uncertain, and the associated capital letters *A*, *B*, *C*, and *D* serve to identify four suggested rotational

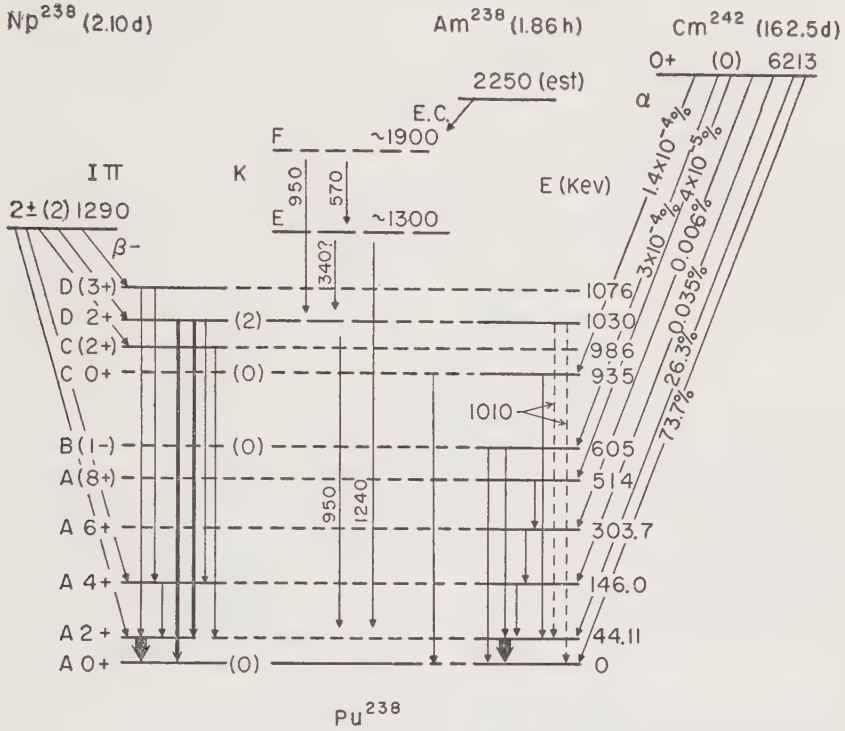


Fig. 3.19 Energy states of Pu^{238} showing suggested rotational bands based on ground and excited states. A description of the various symbols and designations is given in the text. Energy levels are in units of Kev. (Data from F. Asaro, I. Perlman, S. G. Thompson, R. J. Carr, J. O. Rasmussen, H. Slätis, T. O. Passell, F. S. Stephens, Jr., B. Åström, D. Strominger, S. A. Baranov, and K. N. Shlyagin.)

bands. The K quantum number is shown in parentheses. The energies in Kev are given at the right of the levels. Each known level is drawn in the decay schemes of both Np^{238} and Cm^{242} but is dashed in the decay scheme where it is not detectably populated. The placement of the level $C2+$ and its association with the level $C0+$ in a common rotational band is quite tentative. The C and

D bands may be examples of beta- and gamma-vibrational excitations, respectively. The alpha-decay scheme of Cm^{242} going to Pu^{238} is presented again in Fig. 3.20 in a manner such that certain features are segregated for the purpose of greater clarity. The

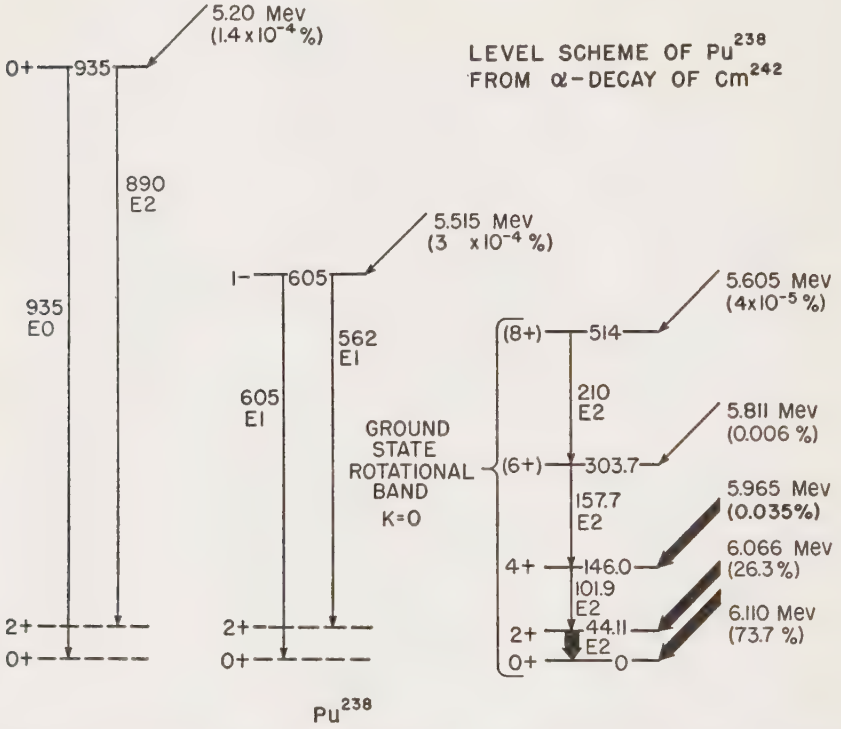


Fig. 3.20 Alpha-decay scheme of Cm^{242} with various components segregated for purpose of clarity.

width of the arrows indicates approximately the transition probabilities.

3.8b Odd-Mass Nuclei

The energy levels of nuclei having an odd number of neutrons or protons are, in general, more complex than those of even-even nuclei and, consequently, have not been worked out with the same degree of certainty. Also, as a group, they show no completely common generalized pattern such as is the case for the even-even

nuclei. As we have mentioned before, nucleonic states are only about 0.1 Mev apart in energy, and vibrational states would be expected some 1 Mev above nucleonic states; hence the situation is involved and the interactions between higher states are expected to be too large for it to be possible to identify individual nucleonic-vibrational-rotational patterns as in even-even nuclides. The alpha transition to the ground state is frequently highly hindered; in some cases it is not observed. Nevertheless, some regularities are observable. In particular, rotational bands of levels rather similar to those of the even-even nuclei have been identified. The principal difference is that the fundamental level of the rotational band favored by alpha decay is usually not the ground state in the case of odd-nucleon nuclei. The general formula for the energies of rotational levels is given by the equation:

$$E_I = \frac{\hbar^2}{2\mathfrak{I}} [I(I+1) + a(-1)^{I+1/2}(I+\tfrac{1}{2})\delta_{K,1/2} - K(K+1)]$$

where $\mathfrak{I}$ = moment of inertia of surface wave motion; I = total angular momentum (nuclear spin) of the level; $\delta_{K,1/2} = 1$ for $K = 1/2$ and $\delta_{K,1/2} = 0$ for $K \neq 1/2$; a is the decoupling parameter which can be determined empirically from the level spacings; and K = spin of base level = component of total angular momentum along the symmetry axis. For odd-A nuclei the quantum states representing collective rotational motion based on a given fundamental level K form the spin sequence:

$$I = K, K+1, K+2, \ldots,$$

all with the parity of the fundamental level. Thus when K is not equal to $1/2$ the level spacing is regular, with the term involving the decoupling factor, a, dropping out, and is determined by the relationship $\frac{\hbar^2}{2\mathfrak{I}} [I(I+1) - K(K+1)]$. This expression applies to even-A nuclei as well as odd-A nuclei and reduces to the simple expression $\frac{\hbar^2}{2\mathfrak{I}} [I(I+1)]$ for $K = 0$, as was mentioned above. It may be emphasized, however, for the case of $K = 0$, that if the intrinsic parity π is even, only even I values appear, and if π is odd, only odd I values are permitted.

The level system for the odd-even nucleus Np^{237} deduced from

the alpha decay of Am^{241}, the beta decay of U^{237}, the electron-capture decay of Pu^{237}, and Coulomb-excitation experiments on Np^{237} represents a particularly good example, as can be seen by considering Fig. 3.21. Eighty-four per cent of the Am^{241} alpha tran-

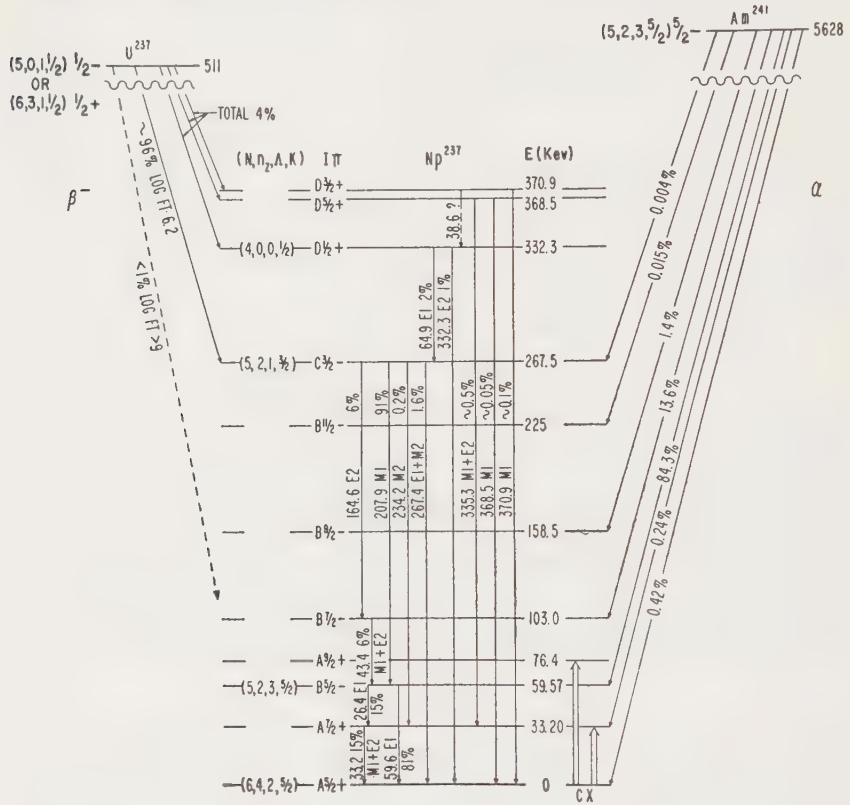


Fig. 3.21 Energy states of Np^{237} showing suggested rotational bands based on ground and excited states. A description of the various symbols and designations is given in the text. Energy levels are in units of Kev. (Data from F. Asaro, I. Perlman, L. L. Gol'din, E. F. Tret'yakov, G.I. Novikova, S. A. Baranov, K. N. Shlyagin, W. G. Smith, J. O. Newton, J. O. Rasmussen, J. M. Hollander, and F. L. Canavan.)

sitions go to a 59.57-Kev level in Np^{237}. This level has nuclear spin and parity 5/2− and is the fundamental level of a rotational band (designated by the letter B) with $\frac{\hbar^2}{2\mathfrak{I}} = 6.19$ Kev. The levels at 103.0, 158.5, and 225 Kev with assignments 7/2−, 9/2−, and

11/2−, respectively, are definitely excited members of this band. The last-named level is reached by only 0.015 per cent of the alpha transitions from Am^{241}. The ground state of Np^{237} has nuclear spin 5/2 but has even parity. The levels at 33.2 and 76.4 Kev are believed to be members of a rotational band (designated by the letter *A*) based on the ground state. J. O. Newton has excited these levels by Coulombic excitation of Np^{237}. The arrows pointing upward denote these induced transitions (designated by CX). The 76.4-Kev level has not been observed in the decay of Am^{241} or U^{237}. The spin sequence for this rotational band is 5/2+, 7/2+, and 9/2+, and the quantum of rotation $\frac{\hbar^2}{2\mathfrak{I}}$ is 4.75 Kev. The gamma transitions following the beta decay of U^{237} in Fig. 3.21 have been well characterized where the transition type is indicated; these data are in agreement with the designated spin and parity assignments. Another rotational band is designated by the letter *D*. Proposed assignments of the asymptotic quantum numbers (N,n_z,Λ) and of the *K*-quantum number are given in parentheses, and the spins and parities are also designated. Thus the low-lying levels of Np^{237} fall neatly into two rotational bands and indicate the essential correctness of the collective model in this mass region.

The alpha-decay schemes of the odd-even nuclei Am^{239} and Am^{243} show a pattern with considerable similarity to Am^{241} as shown in Fig. 3.22. The 48-, 60-, and 74-Kev levels in the daughter nuclei Np^{235}, Np^{237}, and Np^{239}, respectively, each populated most abundantly by alpha decay and each de-excited by an *E*1 gamma transition, seem clearly to be corresponding levels in some common nuclear-structure pattern for these similar nuclides which differ in their constitution only by pairs of neutrons. The levels at 74-, 118-, and 173-Kev in Np^{239} probably constitute a rotational band with spins 5/2, 7/2, and 9/2, respectively, analogous to the rotational band based on the 59.57-Kev level in Np^{237} (see Fig. 3.21).

Since an example of the level scheme for an even-odd nucleus is also worth presenting, Fig. 3.23 shows such a diagram for the nucleus Pu^{239}. This shows the alpha-decay scheme of Cm^{243}, the beta-decay scheme of Np^{239}, and the electron capture decay of Am^{239} to the common daughter nucleus, Pu^{239}. The conventions used here are the same as those used in previous figures. The arrows

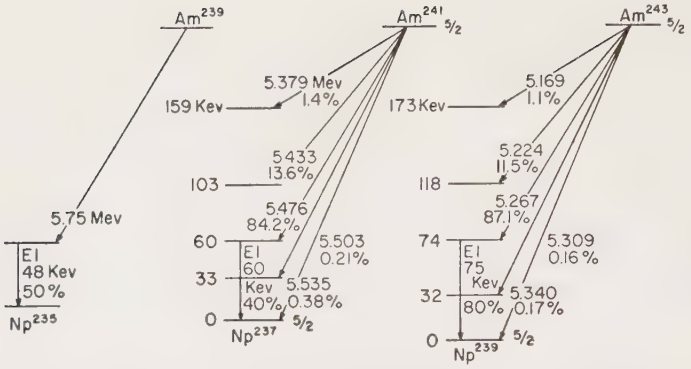


Fig. 3.22 Alpha-decay schemes of analogous odd-even nuclei Am^{239}, Am^{241}, and Am^{243}. (Data from F. Asaro, F. S. Stephens, Jr., I. Perlman, J. P. Hummel, W. M. Gibson, and R. A. Glass.)

are drawn only for experimentally observed transitions, and the widths of the vertical arrows indicate qualitatively the relative gamma transition probabilities. Coulombic excitation is indicated by the symbol *CX*. Proposed assignments of the quantum numbers (N,n_z,Λ,K) are given in parentheses, and the spins and parities are also designated. There is a ground-state rotational band (designated by the capital letter *A*) with the spin sequence 1/2, 3/2, 5/2,

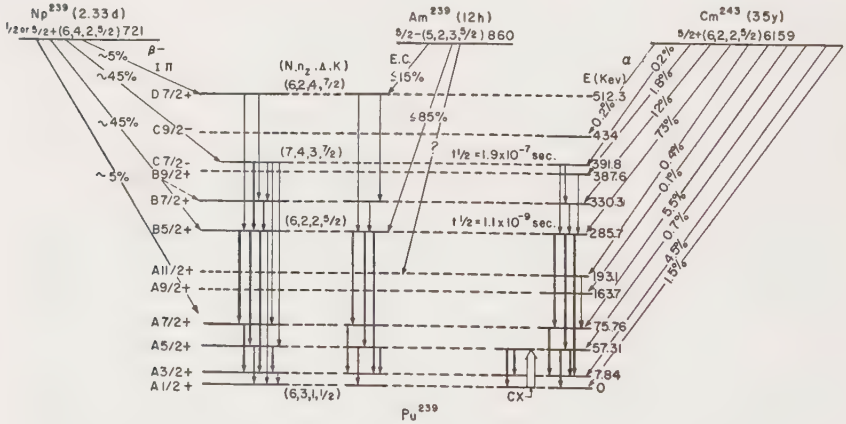


Fig. 3.23 Energy states of Pu^{239} showing suggested rotational bands based on ground and excited states. A description of the various symbols and designations is given in the text. Energy levels are in units of Kev. (Data from J. M. Hollander, W. G. Smith, J. W. Mihelich, W. M. Gibson, F. Asaro, S. Amiel, and J. O. Newton.)

7/2, 9/2, 11/2 and even parity and three suggested members of a rotational band (designated with the capital letter *B*) based on an excited state and with spins 5/2, 7/2, and 9/2 with even parity.

3.8c Additional Comments

The data on odd-odd nuclei are, unfortunately, too sparse to allow any useful correlative treatment at the present time.

Thus we see that in the region of the heavily deformed nuclei, many rotational bands have been identified, not only for even-even nuclei, but also for odd-mass nuclei. Most of these bands have been revealed by alpha spectroscopy, aided by beta and gamma spectroscopy and by Coulomb excitation. Included among the heavy nuclei exhibiting such bands with three or more member levels definitely identified are the following: Em^{218}, Ra^{222}, Ra^{224}, Ra^{226} (2 bands), Th^{226}, Th^{228}, Th^{229}, Th^{230}, Th^{232}, U^{232}, U^{233}, U^{234}, U^{235} (2 bands), U^{236}, Np^{237} (3 bands), Np^{239}, Pu^{238}, Pu^{239} (2 bands), Pu^{240}, Cm^{242}, Bk^{249} (2 bands), Cf^{250}.

3.9 Induced and Spontaneous Fission

3.9a Induced Fission

The property of neutron-induced fission is, of course, an important characteristic of the transuranium nuclides. Many of these undergo fission with slow neutrons, and the cross sections are summarized in Table 3.1. The "Big Three" nuclides U^{233}, U^{235}, and Pu^{239}, which undergo fission with slow neutrons with large cross sections, are the only ones of importance from a practical point of view—that is, nuclear fuels. In the case of a number of the nuclides in the heavy element region, the values of the cross sections for fission, for capture, or for inelastic scattering as a function of neutron energy have also been determined with some care.

An examination of the results shown in Table 3.1 reveals that a large percentage of nuclides which undergo slow neutron fission contain an odd number of neutrons. The addition of a thermal neutron to an odd-neutron nuclide involves the pairing of neutrons. Therefore, the resultant compound nucleus has more excitation energy than the compound nuclei formed from thermal neutron capture on neighboring isotopic even-neutron nuclei. Thus the

observed slow neutron fission of Th^{227}, Th^{229}, Th^{233}, Pa^{230}, Pa^{232}, U^{231}, U^{233}, U^{235}, U^{239}, Np^{234}, Np^{236}, Np^{238}, Pu^{239}, Pu^{241}, Am^{242}, Cm^{243}, Cm^{245}, Cm^{247}, Cf^{249}, and E^{254} is qualitatively in agreement with the prediction of N. Bohr and J. A. Wheeler. In their classical work they calculated the energy required to produce the critical deformation of a heavy nucleus which is needed before it can undergo fission. For the nucleus (Z,A) to be fissionable (that is, be such that fission is able to compete very favorably with other processes of de-excitation) with thermal neutrons, Bohr and Wheeler point out that the binding energy of a neutron to nucleus (Z,A) must exceed the critical deformation energy of the nucleus $(Z,A+1)$. They thus deduced that most of the thermal neutron fission in natural uranium was due to the odd-neutron isotope, U^{235}.

The critical deformation energy corresponds to the potential barrier for fission. Thus with nuclei of odd neutron number especially, the capture of a slow neutron may provide sufficient excitation to overcome the barrier and increase fission probability enough for it to compete with gamma ray emission. Although the fission barrier is a rather qualitative concept, it is evident that spontaneous fission (discussed below) is a barrier penetration phenomenon with a high degree of sensitivity toward the height of the barrier. For example, U^{238} excited to 5.1 Mev, the threshold for photo-fission, has a fission lifetime of about 10^{-14} seconds, a factor approximately 10^{37} times shorter than the fission lifetime of U^{238} in its ground state, which has a spontaneous fission half life of about 10^{16} years. Hence each decrease of about 0.13 Mev in the barrier height or required activation energy corresponds to an increase of the fission rate by a factor of ten.

The theory of Bohr and Wheeler and several subsequent modifications predict a variation of fission barrier or threshold energy which has a rather strong dependence on Z^2/A. However, fission thresholds obtained from photo-fission and neutron-fission thresholds plus neutron binding energies show that these thresholds do not depend so strongly on Z and A as these theories predict. The quantity Z^2/A is known as the "fissionability parameter" and is a measure of the tendency of a nuclide to undergo fission—that is, the larger the value of this parameter, the greater is this tendency. This parameter represents the ratio of nuclear Coulomb repulsive

energy, proportional to Z^2/r, to the stabilizing nuclear surface energy, proportional to the surface area or r^2. The nuclear radius r is proportional to $A^{1/3}$, so this ratio is proportional to Z^2/A.

Some years ago, the author made an attempt to calculate the slow neutron fission threshold, or barrier, E_b, from an empirical equation for spontaneous fission determined from the characteristics of a line like that shown in Fig. 3.32 below, assuming that the form of an equation given by S. Frankel and N. Metropolis, $T = 10^{-21} \times 10^{7.85E_b}$ seconds, governing the dependence of spontaneous fission half life on the fission barrier is approximately correct. This led to the expression $E_b = (19.0–0.36\ Z^2/A)$ Mev. This is applicable only to intermediate compound nuclei of the even-even type because the relationship in Fig. 3.32 applies only to this nuclear type. Since even-odd and odd-even nuclides are retarded in their rate of spontaneous fission decay by an average factor of about 10^3, and odd-odd nuclides have decay rates retarded by a factor of about 10^5, the fission barriers might be higher by about 0.4 Mev and 0.7 Mev, respectively, on the basis that each factor-of-ten increase in half life corresponds to an increase of about 0.13 Mev in barrier height. Thus the relationship becomes

$$E_b = (19.0 - 0.36Z^2/A + \epsilon) \text{ Mev}$$

where $\epsilon = 0$ for even-even nuclides, $\epsilon = 0.4$ for even-odd and odd-even nuclides and $\epsilon = 0.7$ for odd-odd nuclides. Since induced fission can occur at the point below the top of the barrier where the time for fission becomes comparable with the time for gamma emission—that is, in a time of about 10^{-14} seconds—the required energy of activation, E_a, is less than the barrier height, E_b, which represents a hypothetical fission time of some 10^{-21} seconds. Thus if we again use the relationship that each factor of ten in rate corresponds to some 0.13 Mev of energy, it follows that E_a is, in general, some 0.9 Mev less than E_b.

When the energy difference NBE (neutron binding energy) minus E_a (calculated) is tabulated, as in Table 3.15, there results a correlation with slow-neutron fission which is surprisingly good. The nuclides which show a positive energy difference have a fission cross section greater than about one barn, and the nuclides with a negative (NBE minus E_a) energy difference have fission cross sec-

TABLE 3.15 *Correlation of Slow Neutron Fissionability with Activation Energy for Fission and Corresponding Neutron Binding Energy*

NUCLIDE	E_b* (Mev)	E_a** (Mev)	NBE**‡ (Mev)	NBE–E_a (Mev)	SLOW NEUTRON FISSIONABILITY**‡‡
Ra^{226}	7.1	6.2	4.5	−1.7	−
Ra^{228}	7.2	6.3	4.7	−1.6	−
Ac^{227}	7.2	6.3	5.0	−1.3	−
Th^{227}	6.2	5.3	7.1	1.8	+
Th^{228}	6.7	5.8	5.3	−0.5	−
Th^{229}	6.3	5.4	6.8	1.4	+
Th^{230}	6.8	5.9	5.0	−0.9	−
Th^{232}	6.9	6.0	4.9	−1.1	−
Th^{233}	6.5	5.6	6.1	0.5	+
Th^{234}	7.0	6.1	4.6	−1.5	−
Pa^{230}	6.5	5.6	6.7	1.1	+
Pa^{231}	6.8	5.9	5.7	−0.2	−
Pa^{232}	6.6	5.7	6.5	0.8	+
Pa^{233}	7.0	6.1	5.2	−0.9	−
U^{230}	6.2	5.3	5.9	0.6	+
U^{231}	5.9	5.0	7.3	2.3	+
U^{232}	6.3	5.4	5.8	0.4	+
U^{233}	6.0	5.1	6.8	1.7	+
U^{234}	6.4	5.5	5.2	−0.3	−
U^{235}	6.1	5.2	6.5	1.3	+
U^{236}	6.5	5.6	5.3	−0.3	−
U^{238}	6.6	5.7	4.8	−0.9	−
U^{239}	6.3	5.4	5.9	0.5	+
Np^{234}	6.1	5.2	6.9	1.7	+
Np^{236}	6.2	5.3	6.7	1.4	+
Np^{237}	6.6	5.7	5.5	−0.2	−
Np^{238}	6.4	5.5	6.1	0.6	+
Np^{239}	6.7	5.8	5.1	−0.7	−
Pu^{236}	6.0	5.1	6.0	0.9	+
Pu^{238}	6.1	5.2	5.6	0.4	+
Pu^{239}	5.7	4.8	6.4	1.6	+
Pu^{240}	6.2	5.3	5.4	0.1	+
Pu^{241}	5.9	5.0	6.3	1.3	+
Pu^{242}	6.3	5.2	5.0	−0.2	−
Am^{241}	6.3	5.4	5.6	0.2	+
Am^{242m}	6.0	5.1	6.2	1.1	+
Am^{242}	6.0	5.1	6.2	1.1	+
Am^{243}	6.4	5.5	5.2	−0.3	?
Cm^{242}	5.8	4.9	5.6	0.7	?
Cm^{243}	5.4	4.5	6.7	2.2	+

TABLE 3.15 *Correlation of Slow Neutron Fissionability with Activation Energy for Fission and Corresponding Neutron Binding Energy (Continued)*

NUCLIDE	E_b* (Mev)	E_a** (Mev)	NBE**‡ (Mev)	NBE–E_a (Mev)	SLOW NEUTRON FISSIONABILITY**‡‡
Cm^{244}	5.9	5.0	5.7	0.7	?
Cm^{245}	5.5	4.6	6.4	1.8	+
Cf^{249}	5.2	4.3	6.6	2.3	+
E^{254}	5.6	4.7	6.0	1.3	+

* Potential barrier height for fission.

** Activation energy for fission, $E_a = \left(19.0 - 0.36\frac{Z^2}{A} + \epsilon - 0.9\right)$ Mev.

**‡ NBE for nuclide with mass number $A + 1$.

**‡‡ The + denotes cross section for slow neutron fission greater than about 1 barn; the − denotes cross section less than about 1 barn.

tions below this arbitrary line of demarcation for slow-neutron fissionable nuclides. When the value of E_a exceeds the NBE, leading to a negative value for (NBE minus E_a) in Table 3.15, this should be equal to the neutron threshold for fission. Thus the following nuclides should have the indicated thresholds for neutron-induced fission: Th^{232} (1.1 Mev), Pa^{231} (0.2 Mev), U^{234} (0.3 Mev), U^{236} (0.3 Mev), U^{238} (0.9 Mev), and Np^{237} (0.2 Mev). Although such thresholds are not sharp, because of the barrier-penetration nature of the phenomenon, the following approximate values have been experimentally determined: Th^{232} (1.1 Mev), Pa^{231} (0.4 Mev), U^{234} (0.3 Mev), U^{236} (0.6 Mev), U^{238} (0.9 Mev) and Np^{237} (0.3 Mev). It can be seen that the agreement between the predicted and the experimentally determined threshold values is good. Since nuclei can be excited to less than the NBE in d,p reactions, it is possible to determine the value of E_a for slow-neutron fissionable nuclides by measuring the proton energy at the fission threshold for deuterons of known energy. As an example, such an experiment shows that U^{235} undergoes fission at an excitation energy of about 1.2 Mev below that given to it by an added slow neutron, in good agreement with the predicted value of 1.3 Mev suggested by Table 3.15.

Such calculated E_a values using a straight-line dependence of spontaneous fission half lives on Z^2/A can be only approximate at best, because, as will be seen in the discussion of spontaneous fission below, the rate for this process depends on more complicated factors

than such a dependence on Z^2/A. Thus since the derivation of this formula ignores the effect of 152 neutrons on spontaneous fission (see below), it should fail by yielding too large values of E_a for nuclei with more than 152 neutrons. The parameter Z^2/A is derived on the basis of spherical nuclei, while the nuclei in the transuranium region apparently are spheroidal with a prolate shape.

An interesting correlation of slow neutron fissionability can be made by considering the ratio σ_f/σ_c, where σ_f is the thermal neutron fission cross section and σ_c the thermal neutron capture cross section. The ratio of the thermal neutron fission to the thermal neutron capture cross section can be expressed as

$$\frac{\sigma_f}{\sigma_c} = \frac{\Gamma_f}{\Gamma_c}$$

where $\Gamma_f/\hbar$ is the probability per unit time that the compound nucleus loses its excitation by fission, and $\Gamma_c/\hbar$ is the probability per unit time that the compound nucleus loses its excitation by gamma ray emission. If Γ_c is a very slowly changing function of the nuclear excitation energy in the region under consideration (5 to 7 Mev) and if Γ_f is a highly dependent function of nuclear excitation energy in the above energy range, then a correlation of σ_f/σ_c with the energy difference, NBE $- E_a$, would be expected. Of course, nuclear type may influence the σ_f/σ_c ratio to some degree, but it is not possible to take this into account in a quantitative manner. For example, the probability for gamma ray emission may be less for the intermediate fissioning nuclei of the even-even type because of larger level spacing, which means that fission is relatively favored and would occur at lower excitation relative to the barrier height.

Some values of log σ_f/σ_c are plotted in Fig. 3.24 against the energy difference NBE $- E_a$ with E_a calculated as indicated above. It can be seen that the ratio σ_f/σ_c decreases sharply with decreasing values of NBE $- E_a$. Nuclides such as Pa^{231} and Np^{237} are on the borderline of thermal neutron fissionability. Such nuclides are of particular interest, since they indicate that the fission threshold is gradual rather than sharp, in accord with the barrier penetration concept for the fission process.

Among the nuclides in which fission can be induced with low-energy neutrons, the fission cross section varies widely with neutron

energy. Fig. 3.25 illustrates this for the important, slow-neutron fissionable nuclides U^{233}, U^{235}, and Pu^{239}. These curves represent the composite data as compiled in the Brookhaven Neutron Cross Sections Report by D. J. Hughes and R. B. Schwartz from results reported by American, European, and USSR laboratories. The

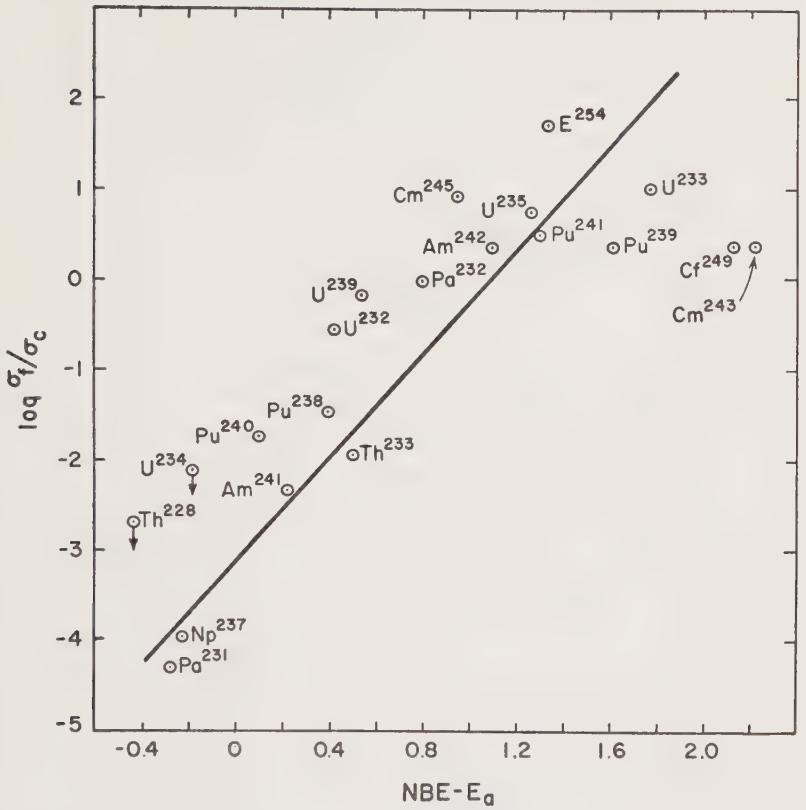
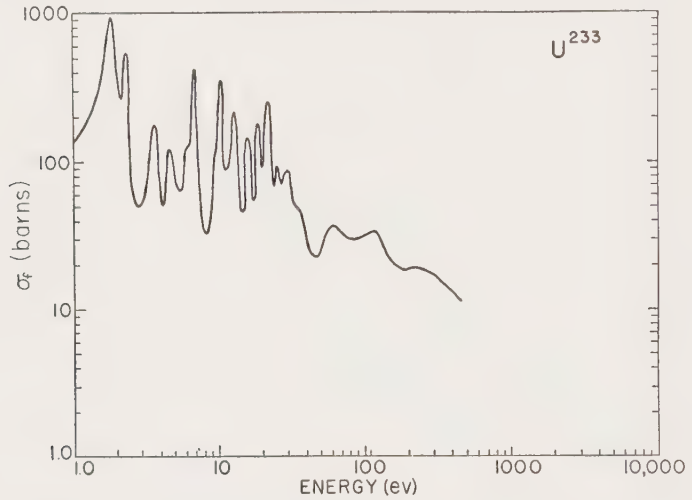
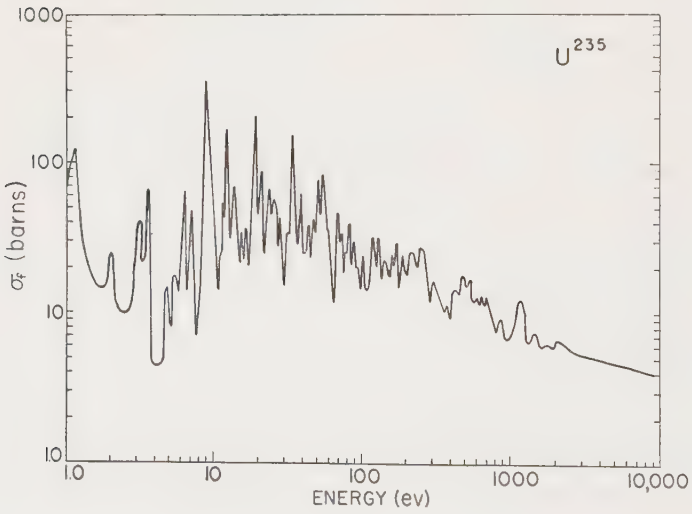


Fig. 3.24 Plot of comparative slow-neutron fissionability. σ_f/σ_c denotes ratio of slow neutron fission to n,γ cross section. (♀ signifies upper limit, $NBE - E_a$ denotes difference between neutron binding energy and activation energy for fission.

sharp peaks in the curves are the "resonances" and are due to the capture of a neutron with kinetic energy such that the binding energy plus the kinetic energy of the neutron is very close to the energy of some level in the excited nucleus. On theoretical grounds it can be shown that the cross section should approach a maximum

when this excitation energy of the neutron is very close to the energy of some level in the excited nucleus. The resonances correspond to energy levels about 6 Mev above the ground level in the compound nucleus systems. The same resonances appear in both fission and neutron capture, but the value of α, the ratio of the neutron capture to the neutron fission cross section, varies for the resonances; the exact nuclear data for these resonances is very important for reactor





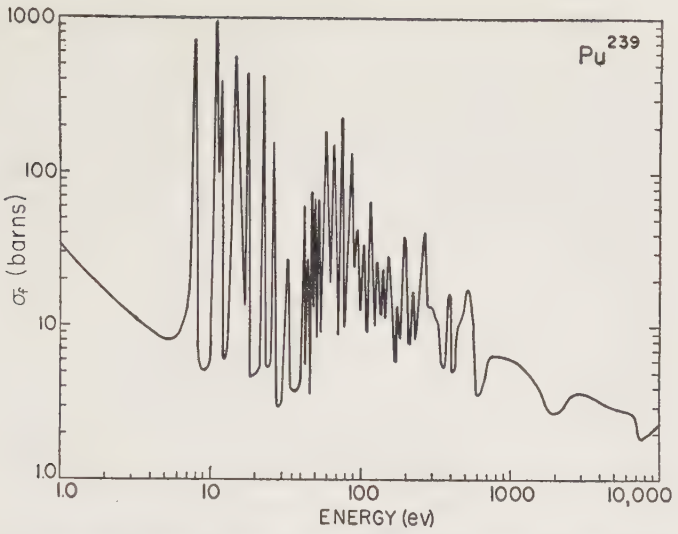


Fig. 3.25 Variation of fission cross section with neutron energy for U^{233}, U^{235}, and Pu^{239}.

design. In the case of U^{235} the average spacing of the resonances is only about 0.7 electron volts in the region of 0.2 to about 60 electron volts. A very important resonance from the standpoint of reactor design occurs for Pu^{239} at the low neutron energy of 0.296 electron volts; the value of α for this resonance is quite high, 0.69. The comparable probabilities for the n,γ and fission reactions were a great surprise when first discovered, indicating a time for slow neutron fission of some 10^{-14} seconds.

We have seen that with thermal neutrons we can induce fission in those nuclides whose neutron binding energies are sufficiently high so that when the neutron is captured the excitation energy of the resulting nucleus is above the fission threshold. As mentioned above, with higher energy neutrons we can induce fission in nuclides which do not fission with thermal neutrons. As an example of the variations of fission cross section with energy for such nuclides, Fig. 3.26 shows data for Th^{232}, U^{236}, and U^{238}, which are typical for many nuclides undergoing fission in the region above a few hundred kilovolts. (The data for Th^{232} and U^{236} came from the Brookhaven compilation of neutron cross sections by D. J. Hughes and J. A. Harvey and that for U^{238} from the work of R. K. Smith, R. L. Henkel, and R. A. Nobles of the Los Alamos

Scientific Laboratory.) The observed smooth variation of the cross sections with energy is expected from the fact that the nuclei have sufficiently high excitation energies so that the detailed properties of individual nuclear states are unimportant and statistical concepts are applicable. Peaks of the type seen in the curves for Th^{232}

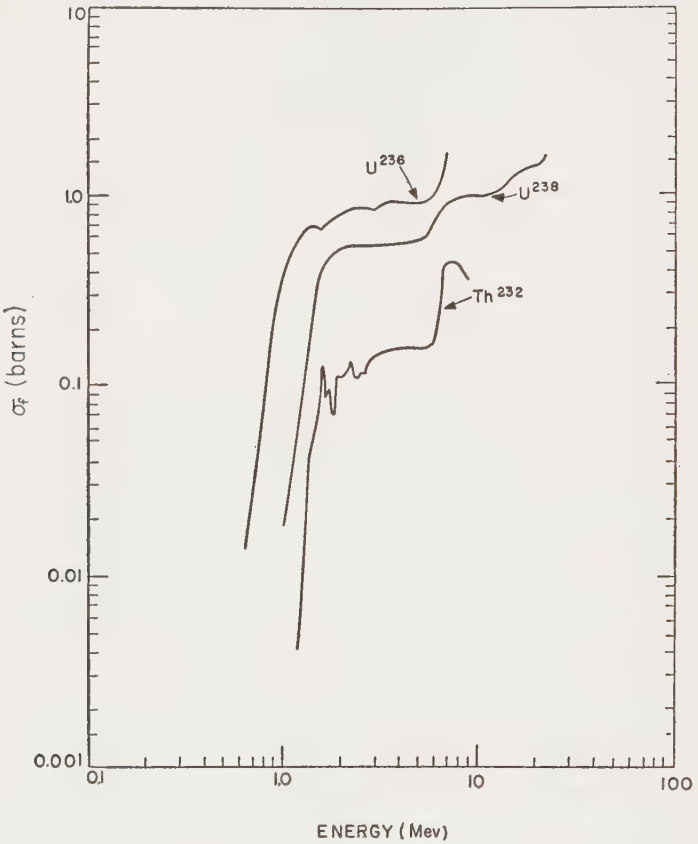


Fig. 3.26 Variation of fission cross section with neutron energy for Th^{232}, U^{236}, and U^{238}.

and U^{236} can be explained as follows. The rise in the cross section is due to the availability of a new fission channel in the transition state (see below) and the drop is due to the availability of a new channel for inelastic neutron scattering. The typical rise of the cross section to a higher level above about 6 to 8 Mev is due to the fact that the excited compound system can emit a neutron and

leave the residual nucleus with an excitation above its fission threshold, in which case the system gets a second chance to undergo fission; the subsequent rises in the curve for U^{238} are explained in the same way. The excitation functions for the fission of the slow neutron fissionable nuclides U^{233}, U^{235}, and Pu^{239} are also of interest; the data of Smith, Henkel, and Nobles of the Los Alamos Laboratory are shown in Fig. 3.27, which also includes a curve for U^{238}

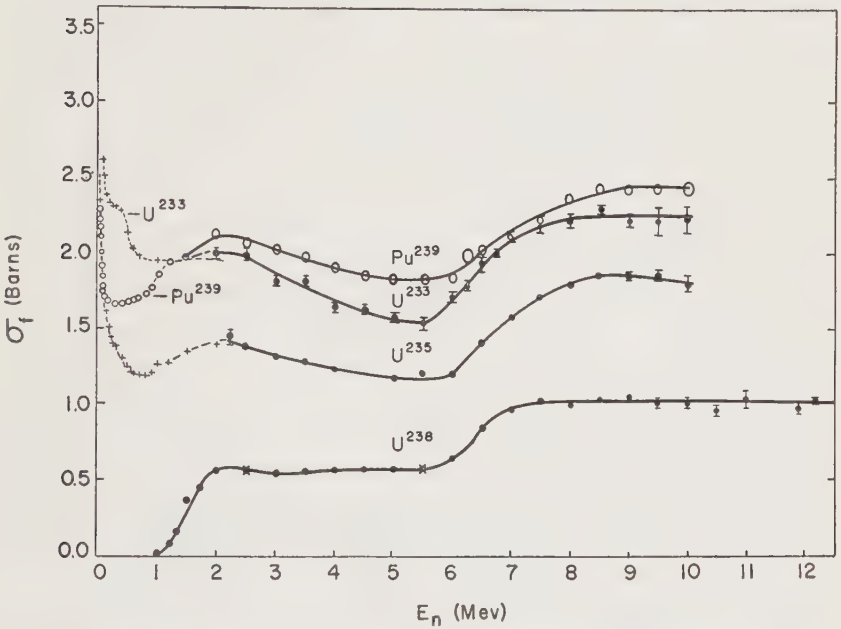


Fig. 3.27 Variation of fission cross section with fast neutron energy for U^{238}, U^{233}, U^{235}, and Pu^{239}.

for purposes of comparison. It may be seen that the behavior is similar to that for the non-slow-neutron fissionable nuclides, except that, rather than exhibiting a threshold, the curves are shown coming down at the beginning from the high values at slow neutron energies.

We find that we need only to find some way to excite the nucleus in order to induce fission. Neutrons, photons, protons, mesons, deuterons, and helium ions and heavier ions have all been used to cause fission of the heavy elements. Determination of the threshold

energy for fission can give the activation energy, in the cases of neutron- or photon-induced fission. The threshold for photofission gives the activation energy directly, while the fast neutron fission threshold plus the neutron binding energy (discussed above) gives the same quantity. The fission thresholds determined in these ways cannot be sharp because of the barrier penetration nature of the phenomenon, and hence only approximate values can be expected. The following thresholds have been determined for photofission: Th^{232} (5.4 Mev), U^{233} (5.2 Mev), U^{235} (5.3 Mev), U^{238} (5.1 Mev), and Pu^{239} (5.3 Mev). It is interesting to note that the method outlined above leads to the following activation energies: Th^{232} (5.5 Mev), U^{233} (5.4 Mev), U^{235} (5.5 Mev), U^{238} (5.3 Mev), and Pu^{239} (5.2 Mev). The agreement between the experimental and the predicted values is quite good.

In addition to the correlation of fissionability with Z^2/A for slow neutron fission it appears that such a correlation is applicable for higher energies to the heaviest elements, thorium and above. For example, J. R. Huizenga has examined the data on the relative probabilities for gamma-induced fission and γ,n reactions in the region of gamma energies of some 5 to 10 Mev, and Huizenga and R. E. Batzel have examined the relative probabilities for neutron induced fission and $n,n\gamma$ reactions in the region of neutron energies of several Mev. In each case it appears that $\Gamma_f/\Gamma_{\text{total}}$ or Γ_f/Γ_n increases with Z^2/A. Also, the cross sections for certain spallation reactions induced with charged particles, discussed in Section 3.1b, are a sensitive measure of the competition between fission and neutron emission—that is, give a measure of the relative probabilities for fission and neutron emission at several stages in the reaction process. There has been some success in correlating these cross sections with the fissionability parameter Z^2/A and the neutron-binding energies; this would indicate that the parameter Z^2/A gives a measure of the relative tendency to undergo fission, and hence of Γ_f/Γ_n, in nuclides with excitation in the region of 20 to 40 Mev and higher energy.

The competition between fission and neutron emission, represented by Γ_f/Γ_n, is of interest whenever the nucleus has been excited sufficiently for either reaction to take place. The variation of Γ_f/Γ_n with the excitation energy is of particular interest. Since

fission thresholds are in general lower than neutron-binding energies in the region of the heaviest elements the ratio of Γ_f/Γ_n must, of course, decrease rapidly as the excitation energy is increased above the neutron-binding energy. The flat portions of the excitation functions for the fission of nuclides with fast neutrons indicate that the ratio Γ_f/Γ_n does not vary much with excitation energy in the range from a few Mev above the neutron-binding energy up to some 20 Mev; see especially the curve for U^{238} in Fig. 3.26 but also the other curves. Also, analysis of excitation functions for spallation reactions induced with charged particles as described in Section 3.1b, leading to the conclusion that fission and neutron emission compete at each step of an evaporation chain, gives the result that the ratio Γ_f/Γ_n for this range of excitation energy, some 20 to 40 Mev, is not strongly dependent on the energy. On the other hand, there is some evidence that the ratio Γ_f/Γ_n tends toward smaller values in the excitation energy region of hundreds of Mev or higher. Γ_f, dependent on Z^2/A, varies inversely as A and Γ_n, dependent on neutron binding energy, varies directly as A; hence the ratio Γ_f/Γ_n should decrease with increasing A, in agreement with experiment. R. Vandenbosch, T. D. Thomas, S. E. Vandenbosch, R. A. Glass, and the author have suggested methods for calculating approximate values of Γ_f/Γ_n in the excitation energy range below about 40 Mev from the yields of spallation reactions. Such treatment of the yield data from helium-ion-induced reactions on U^{235} and U^{238} gives the indicated values of Γ_f/Γ_n for the following compound nuclei: Pu^{235} (10), Pu^{236} (3.8), Pu^{237} (5.7), Pu^{238} (2.1), Pu^{239} (3.3), Pu^{240} (1.3), Pu^{241} (1.9), and Pu^{242} (0.75). Other examples of values of Γ_f/Γ_n deduced from the yields of similar spallation reactions are: U^{236} (0.43), U^{232} (1.6), Cm^{238} (7.1), and Fm^{252} (3.9).

Measurements of the mass distribution of the fission fragments show that for the fission of a nucleus with low excitation the production of fragments with unequal mass—that is, asymmetric fission, is the most probable. In Fig. 3.28 is shown the mass distribution of the products from the thermal neutron fission of U^{233}, U^{235}, and Pu^{239}. We see that the nucleus splits predominantly into two fragments of unequal mass, the phenomenon known as asymmetric fission. In spontaneous fission the asymmetry is even more pronounced than in thermal neutron-induced fission. Such dependence

of fission product yield upon mass number can be determined by radiochemical and mass spectrometric methods and shows fine structure, related to closed shells in the fission product nuclei, when plotted on a larger scale. These "spikes," corresponding to enhanced fission yield, are apparently due to closed-shell effects, such as modes of fission in which one of the primary fragments has a closed shell of neutrons or protons or in which there are fission products with the boil-off of a neutron or two present in excess of a closed shell. When the mass-yield curves of different fissioning nuclei are compared, it is found that, with increasingly heavier nuclei, the position of the heavy mass peak remains rather constant,

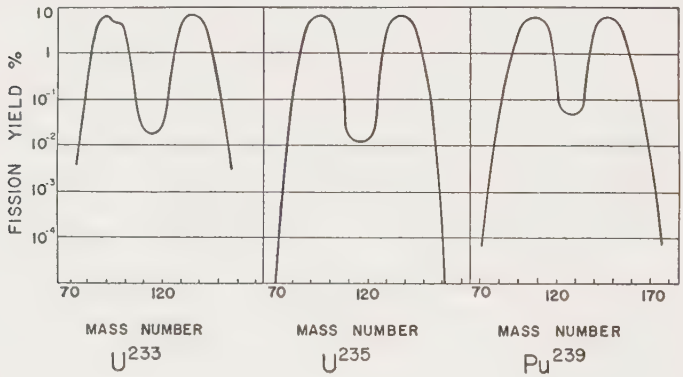


Fig. 3.28 Distribution of fission product yield with mass number for slow neutron fission of U^{233}, U^{235}, and Pu^{239}. ("Spikes" in curves, due to effect of closed shells, are not shown.)

the light peak moving up to higher mass values. The fission products have an excess of neutrons and are removed from beta stability, on the average, by a beta-decay chain length of about three members, although there is a distribution of "independent yields" along the chain. (In low energy fission the beta-decay average chain lengths increase for the following nuclides in the order U^{233}, Pu^{239}, U^{235}, Th^{232}, and U^{238} until the average length is about four members for U^{238}.) The "Equal Charge Displacement" hypothesis of L. E. Glendenin, C. D. Coryell, and R. R. Edwards suggests that the beta-decay chain lengths of the two complementary fission products in slow neutron fission are equal. A. C. Pappas has made a slight modification of this hypothesis in which he considers shell effects

and primary fragments before prompt neutron emission in calculating the nearly equal chain lengths.

As the excitation energy of the compound nucleus is increased, the valley between the two peaks in the mass yield curve rises, as

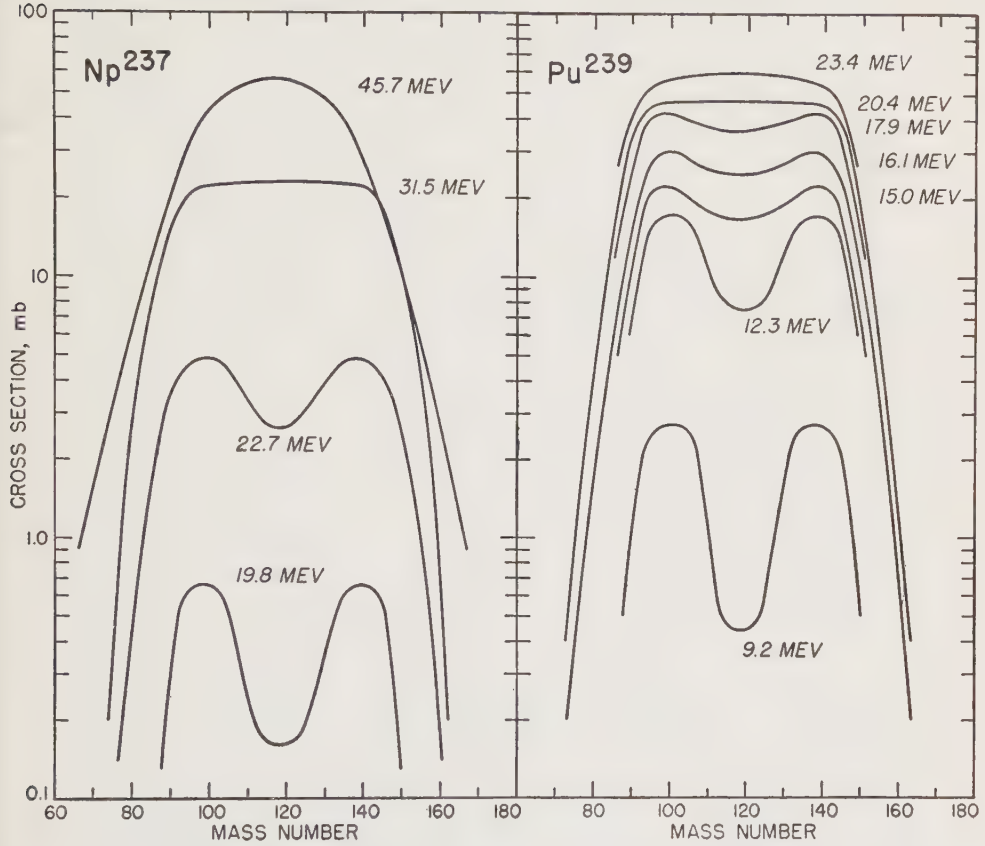


Fig. 3.29 Distribution of fission product yield with mass number for fission induced in heavy elements with helium ions (on Np^{237}) and deuterons (on Pu^{239}) of various energies. (Data of W. M. Gibson, R. A. Glass, and the author.)

shown in Figs. 3.29 and 3.30, implying that as the excitation energy of the fissioning nucleus increases, symmetric fission becomes more probable. At still higher energies, the symmetric mode of fission continues to predominate and the wings of the fission-yield distribution curves rise. (In the Bev energy region the "fragmentation"

process contributes to the yield of products in a manner similar to the fission process as mentioned in Section 3.1b. For example, N. A. Perfilov and co-workers have found that in the case of uranium bombarded with 600 Mev protons about one per cent of the fissions are preceded by fragmentation with the emission of products with

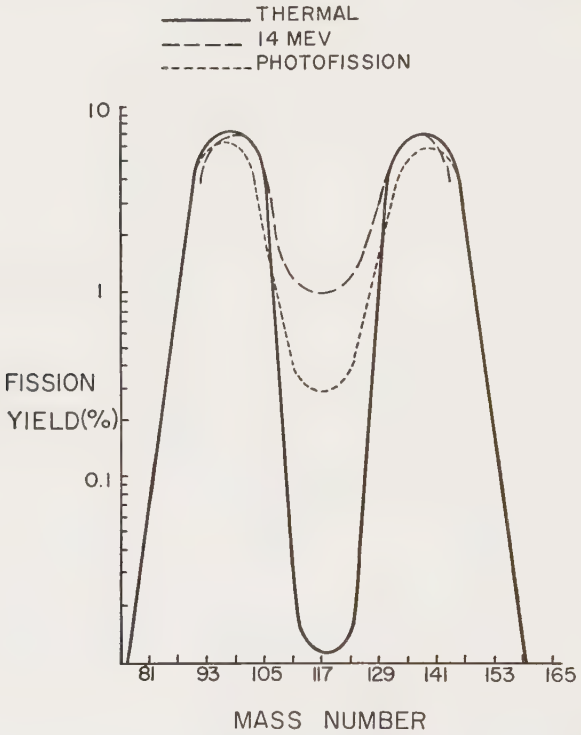


Fig. 3.30 Fission yields from U^{235} for the cases of thermal neutron, photofission with 12–16 Mev photons, and 14-Mev neutron fission. "Spikes" in curves, due to effect of closed shells, are not shown. (Data for photofission and 14-Mev fission from J. Barnes, P. B. Elkin, J. Gilmore, M. Melnick, C. Minkkinen, B. Pollock, J. Sattizahn, and R. W. Spence.)

atomic number about 4 to 10, as observed by the observation of three-pronged stars in especially sensitive photographic emulsions.) We see from the curves shown in Figs. 3.29 and 3.30 that for fissioning nuclei of about the same excitation in the very heavy element region, regardless of how the excitation has been produced, the degree of asymmetry is about the same. Since fission at many

degrees of excitation from the threshold at 5 to 6 Mev up to about the energy of the incident projectile is probably taking place, depending on the stage of spallation at which the fission occurs, each of the curves can be considered to be the summation of many ranging continuously from nearly the extreme slow-neutron double-humped to the extreme (at least at the highest energies) single-humped shapes. It is interesting to note that for fission of the heaviest elements in the energy range up to some 50 Mev, corresponding to the emission of up to six to eight neutrons, the fission still generally precedes the neutron emission process in the transuranium region, where Z^2/A and hence Γ_f/Γ_n is sufficiently large. Thus fission generally occurs at high excitation energy, and this is associated with symmetric fission. At slightly lower values of Z^2/A (immediately below the transuranium region) sufficiently low values of Γ_f/Γ_n are found so that neutron emission can precede fission and thus more asymmetric fission, due to the lower excitation energy, can occur. The fission of Ra^{226} with 11-Mev protons investigated by A. W. Fairhall and R. C. Jensen, leads to a triple-humped curve, indicating that both asymmetric and symmetric fission are occurring. On the view that asymmetric fission occurs only at low excitation energy, this type of fission disappears for a value of Z^2/A equal to about 35 (corresponding to the region around the compound nucleus thorium), where low energy fission can no longer take place.

In high energy fission the primary fission fragments tend to have the same neutron to proton ratio as the fissioning intermediate nucleus and hence the beta-decay chain lengths are shorter for the heavy fission products which include neutron deficient products in good yields, and therefore independent yields are more important than in slow neutron fission.

Considerable work has been done on determining the kinetic energies of the fission fragments. Because momentum is conserved, it is possible to calculate from the observed energies of a pair of fragments the total kinetic energy released and the masses of the fragments in neutron-induced or spontaneous fission. Calculations have been made as to the charge distribution of the fission fragments on the basis of these measurements. The principal methods of determining the energies of fission fragments are the measurement

of the ionization produced by the fragments, the measurement of the deflection of the fragments as they move through a magnetic field, the measurement of the velocity of the fragments by time-of-flight methods, the calorimetric measurement of the energy, and the use of photographic emulsions to determine the range and energy. Such measurements show that the distribution of kinetic energy between the two fragments is a very complicated matter. The spread in total kinetic energy for the entire distribution of fission products is some 50 Mev. The spread in total kinetic energy at each mass ratio is also very large and can amount to about 50 Mev, and the distribution curve for the total kinetic energy at a given mass ratio can have a half width of 10 to 13 per cent at half maximum. Thus a coincidence measurement of the energy of the fragment pairs is needed to obtain the total energy or mass distribution in any fission event. The most probable mass ratios for fission with slow neutrons are 1.49 for U^{235}, 1.60 for U^{233}, and 1.32 for Pu^{239}. The most probable total kinetic energy of the two fission fragments, for the fission of a given nuclide, seems to be greater for the nearly symmetric than for the symmetric or more asymmetric modes of fission. The data on the masses of the fission products are not sufficiently accurate to indicate definitely whether there is more energy available for asymmetric than for symmetric fission, although there are indications that this is the case. In comparing various nuclei to each other there is a general trend toward increasing total kinetic energy and symmetry of fission as the charge of the fissioning nucleus is increased. As examples, the average total kinetic energy of the fragments from the fission of U^{235} with slow neutrons is 167 Mev, while the total energy of the most probable mode of spontaneous fission of Cf^{252} is 186 Mev. It is difficult to make detailed energy balances to account for all of the energy in the various modes of fission for the neutron-induced or spontaneous fission of a given nuclide.

When the particle inducing the fission has appreciable kinetic energy, the fission products may have an anisotropic distribution in angle. Such anisotropy is observed in fission induced by neutrons, photons, and charged particles, with the precise form depending on the type of fissioning nucleus, the mass ratio of the fragments, and the bombarding energy. With charged particles of

a given energy the anisotropy decreases with Z^2/A. The experimental results indicate that the greatest anisotropies, and the most rapid variations in the anisotropy with energy, occur when the fissioning nucleus is excited to an energy near the fission barrier. A. Bohr has introduced the useful concept for low energy fission of the quantization of nuclear states at the saddle point configuration, as will be described in a little more detail later in this section. The spectrum of states at the saddle point is expected to be qualitatively similar to the ground-state spectrum of a spheroidal nucleus of the particular odd or even type considered, and the K quantum numbers of the saddle-point states play a decisive role in the angular anisotropy. A success of the concept is the interpretation of some of the angular distribution results for fission induced by photons, fast neutrons, or charged particles.

Another aspect of fission that has proved very important and interesting is the average number of neutrons, $\bar{\nu}$, emitted in fission, a quantity which, for low energy fission, ranges from two to four, and η, the average number of neutrons emitted per neutron captured. Table 3.16 lists the values of $\bar{\nu}$, η, and α (the ratio of the

TABLE 3.16 *Values for $\bar{\nu}$, η, and α for the Big Three Fissionable Nuclides with Neutrons of 0.025 Electron Volts (2200 meters/sec)*

NUCLIDE	$\bar{\nu}$	α	η
U^{233}	2.52 ± 0.03	0.105 ± 0.007	2.28 ± 0.02
U^{235}	2.47 ± 0.03	0.192 ± 0.008	2.07 ± 0.02
Pu^{239}	2.91 ± 0.04	0.39 ± 0.03	2.09 ± 0.02

cross section for the radiative capture of the neutron to the cross section for neutron-induced fission) for the "Big Three" fissionable nuclides, U^{233}, U^{235}, and Pu^{239} for neutrons of 0.025 electron volts energy (corresponding to a velocity of 2,200 meters per second). The value for α varies from one resonance peak to another; it decreases with increasing neutron energy so that, for example, it has the value of about 0.07 for U^{235} plus one Mev neutrons. The decrease of α with neutron energy is important in the design of breeder reactors, suggesting the feasibility of the fast neutron breeder in the case of the U^{238}-Pu^{239} cycle, where the value of α is too large to make such a breeding cycle possible for slow neutrons.

TABLE 3.17 *Average Number of Neutrons Released in Fission,* $\bar{\nu}$

ISOTOPE	$\bar{\nu}$	MODE OF FISSION
Pu^{236}	1.89 ± 0.20	sf*
	2.30 ± 0.19	sf
Pu^{238}	2.04 ± 0.10	sf
	2.33 ± 0.08	sf
Pu^{240}	2.257 ± 0.046	sf
	2.02 ± 0.11	sf
Pu^{241}	2.91 ± 0.10	n*
	2.98 ± 0.21	n
Pu^{242}	2.26 ± 0.13	sf
	2.18 ± 0.09	sf
Cm^{242}	3.0 ± 0.3	sf
	2.65 ± 0.09	sf
	2.33 ± 0.10	sf
Cm^{244}	2.60 ± 0.12	sf
	2.84 ± 0.09	sf
Cf^{252}	3.82 ± 0.12	sf
	3.53 ± 0.15	sf
Fm^{254}	4.05 ± 0.19	sf

(data from more than one group of investigators are listed for all nuclides except Fm^{254})
* sf = spontaneous fission, n = slow neutron fission.

Table 3.17 lists the values of $\bar{\nu}$ for spontaneous fission (discussed below) and slow neutron-induced fission of a number of the transuranium elements, and Fig. 3.31 shows the distribution in the number of neutrons for the 80-Kev neutron fission of U^{235} and Pu^{239} and the spontaneous fission of Pu^{240}, Cm^{242}, and Cf^{252}. It may be noted that the curves for Pu^{240} are similar, whether the neutrons come from spontaneous fission or from the compound nucleus during the low energy neutron fission of Pu^{239}. The neutrons appear to come off in the direction of travel of the fission fragments, indicating that they are emitted after scission of the nucleus. (There is some evidence that in slow neutron fission more neutrons are emitted from the light than from the heavy fragments, and that more neutrons are emitted from the heaviest light and heaviest heavy fragments than from the light part of these distribution peaks.)

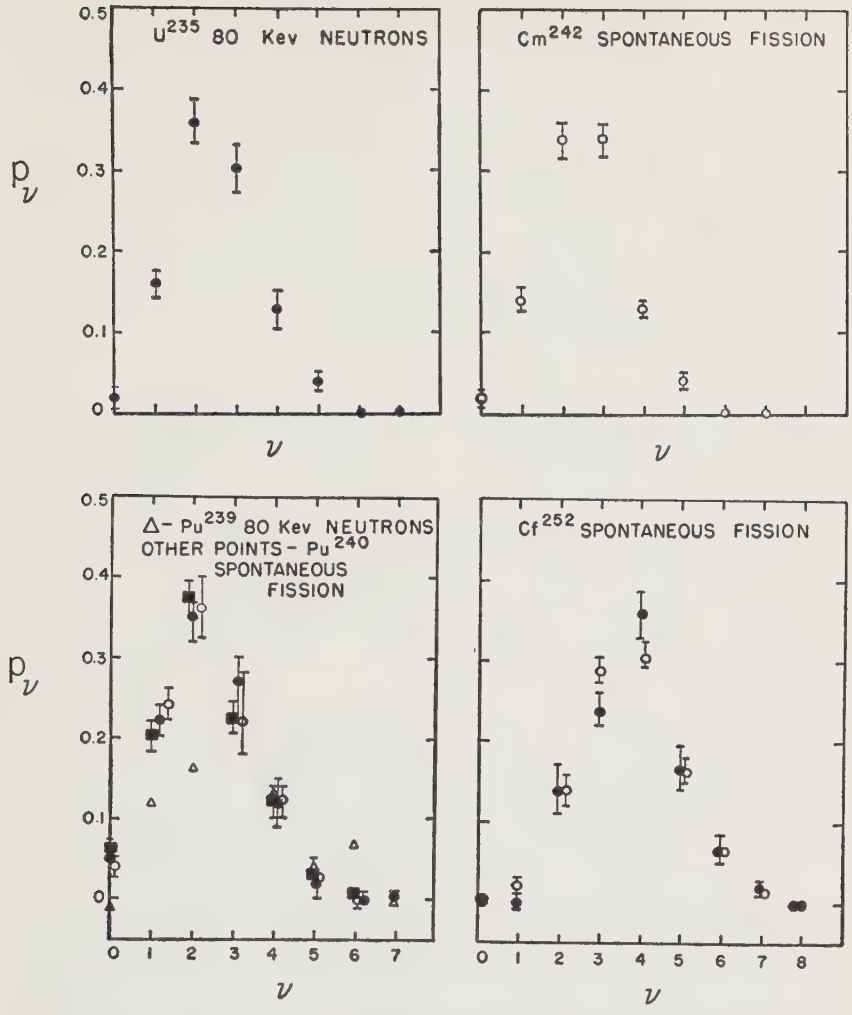


Fig. 3.31 Probability, $P\nu$, for neutron emission versus number of neutrons, ν, for 80-Kev neutron fission of U^{235} and Pu^{239} and spontaneous fission of Pu^{240}, Cm^{242}, and Cf^{252}, according to R. B. Leachman. There is an additional point △ not shown at $\nu = 3$ and $P\nu = 0.55$. (Data from: ● and △, B. C. Diven, H. C. Martin, R. F. Taschek, and J. Terrell; □, J. E. Hammel and J. F. Kephart; ○, D. A. Hicks, J. Ise, Jr., and R. V. Pyle.)

Measurements of the actual number of neutrons emitted in a particular slow fission event show that as few as zero and as many as eight neutrons can be emitted; however, the most probable number is very close to $\bar{\nu}$. The value of ν does not vary appreciably with the mass ratio of the fission fragments, with a slight increase as symmetric fission is approached. Studies of the kinetic energies of neutrons emitted in fission show that the energies of the neutrons range as high as 17 Mev with an average energy of about 2 Mev. It has been found empirically that the neutron energy spectrum fits approximately a curve given by the expression

$$N(E) = k[\sinh (2E)^{1/2}]e^{-E},$$

where $N(E)$ is the number of neutrons emitted with energy E. It has been observed that there is a correlation between the number of neutrons emitted in fission and the kinetic energy of the fission fragments; as the energy of the fragments increases, the number of neutrons decreases. (It is possible to correlate in a rough way the neutron multiplicity and energy distributions with the observed distribution of fragment kinetic energies through neutron evaporation considerations together with the use of values for the masses of the fissioning nucleus and the fission products, as has been done by R. B. Leachman.) The value of $\bar{\nu}$ increases with increasing Z or A of the fissioning nuclide; a study of Table 3.17 shows that $\bar{\nu}$ increases linearly with A. The prompt neutrons are emitted in less than about 10^{-14} seconds, but several tenths per cent (in the slow neutron fission of U^{233}, U^{235}, and Pu^{239}) of the neutrons are delayed, with half lives of fractional seconds to about a minute, and these are emitted in connection with fission product decay chains. The percentage of delayed neutrons is greater, amounting to some 5 per cent in the case of Th^{232} and U^{238}. (A number of delayed neutron emitters with half lives greater than a second have been identified with the decay of bromine and iodine isotopes.) Prompt gamma rays, of total energy amounting to some 10 Mev, are also emitted in the fission process. Alpha particles with energies up to about 30 Mev are also emitted in about 1 in 400 fission events.

With regard to the general aspects of fission, we may conclude that the N. Bohr and J. A. Wheeler approach involving the formation of a compound nucleus with the excitation energy distributed

in a statistical manner among the nucleons still gives the best qualitative picture of fission. In detail, this liquid drop model is not completely satisfactory, in common with a number of other models. However, the consequences of the liquid drop model of fission have not, so far, been worked out in a quantitative and comprehensive manner. In particular, it is not known how even an idealized, uniformly charged, classical drop would divide, as, for example, whether symmetric or asymmetric fission would be preferred in a given set of circumstances. A prerequisite of a theory of the division of a liquid drop is a knowledge of the potential energy of deformation of the system. Some information on the deformation energy of a uniformly charged drop is available, mainly from the work of Bohr and Wheeler; R. D. Present and J. K. Knipp; S. Frankel and N. Metropolis; V. L. Businaro and S. Gallone; V. G. Nossoff; and W. J. Swiatecki. At the present time the calculations are not yet sufficiently comprehensive to serve as a basis for a theory of the division of a drop. In particular, information on the deformation energy of asymmetric shapes is very limited. In spite of this, attempts have been made to find a direct connection between the phenomenon of asymmetry and some simple physical property of nuclei.

A number of such explanations of asymmetric fission have been advanced. M. G. Mayer and L. Meitner and D. Curie have suggested independently that the asymmetry is due to a tendency of the nucleus to fission to a pair of fragments, one of which has a closed shell of neutrons and protons. D. L. Hill and J. A. Wheeler have proposed an explanation that as the nucleus is deformed, the gerade levels, having wave functions symmetric to reflection in the equatorial plane, are pushed to higher energies, with the result that further deformation is possible only if the nucleus can slip from the *gerade* levels to the lower energy *ungerade* levels. According to Hill and Wheeler, such slippage is facilitated only if the nucleus is asymmetrically deformed. V. I. Frenkel has suggested that, because of its lower reduced mass, a nucleus in an asymmetric deformation can penetrate the fission barrier more readily than can one in a symmetric deformation, but Hill and Wheeler have taken issue with this explanation.

P. Fong has attempted an explanation for asymmetric fission

in terms of the masses of the fission fragments. He argues that, because of shell effects, the masses of the asymmetric fragments will be lower than those of the symmetric fragments. The result is that the asymmetric fragments will have a higher excitation energy, and, hence, a higher level density than the symmetric. If, as Fong assumes, fission is a slow enough process so that equilibrium is established among the various possible states at every moment during fission, there will be more nuclei passing through the configurations having high level densities—that is, the asymmetric configurations.

A discussion of the problem by A. Bohr throws light on certain aspects of fission. As the excited nucleus approaches the saddle point (the highest energy point along the energetically favorable reaction path leading to fission), its excitation energy is converted into potential energy of deformation, with the result that at the saddle point the nucleus is "cold." Only a few widely spaced levels will be available to the nucleus, and the spins and parities of these levels will probably have a marked effect on the mode of fission. It is thought that the spectrum of low-lying odd-parity states in even-even nuclei of the heavy elements can be explained by assuming that the nucleus is "pear-shaped." If the spectrum of levels at the saddle point is to be similar to that near the ground-state configuration, the nucleus will probably also have a pear-shaped, or asymmetric, mass distribution as it passes over the saddle point. (At higher excitation energies, levels which do not involve an asymmetric shape for the nucleus will become available, and fission will become more symmetric.) As an example of this we shall consider the photofission of an even-even nucleus by a gamma ray having an energy equal to the height of the fission barrier. The excitation will be predominantly by an electric dipole transition and therefore the spin of the nucleus must be unity with odd parity. The lowest $1-$ state at the saddle point is probably that having $K = 0$, analogous to that in the ground-state spectrum mentioned earlier (Section 3.6a), and, therefore, it is expected that this state will play the major role in the reaction. The angular momentum vector of the photon lies along its direction of motion, since it is a transverse wave, so that the total angular momentum of the compound nucleus must also point in this direction. Since the angular momentum vector of the $1-$, $K = 0$ state is perpendicular to the

nuclear symmetry axis (the angular momentum 1 comes from rotation about an axis perpendicular to the direction of motion of the photon), the maximum in the angular distribution of the fission fragments will, therefore, be in this direction. The angular distribution calculated from this theory shows that the intensity at angle θ to the direction of the photon is proportional to $\sin^2 \theta$. This result is in good accord with experiment. Since the wave function of the $1-$, $K = 0$ state is antisymmetric in the coordinates describing symmetry of the nuclear shape, a nucleus in this state cannot undergo symmetric fission. The limited experimental evidence on this point is also in agreement with this interpretation. In the case of U^{235}, with ground-state angular momentum equal to 7/2, more channels are offered for photofission, which is, perhaps, in agreement with the observed isotropic distribution of fission fragments in this case.

3.9b Spontaneous Fission

Spontaneous fission is generally observed in the region of thorium and above and becomes an increasingly important mode of decay until by the time fermium is reached, its rate for some isotopes becomes comparable to that of other radioactive modes of decay. This phenomenon was first observed, in natural uranium, by G. N. Flerov and K. A. Petrzhak in the USSR in 1940. Spontaneous fission is a barrier penetration phenomenon and a crude method for estimating the barrier height, E_b, was given above. Alternatively, the relationship $T = 10^{-21} \times 10^{7.85E_b}$ can be used to calculate E_b (in Mev) in each case where the value of T, the half life for spontaneous fission (in seconds) is known. The rate of spontaneous fission increases about a factor of ten for each decrease of 0.13 Mev in barrier height, on the basis of the dependence discussed above (Section 3.9a). The data on the spontaneous fission for heavy nuclides are summarized in Table 3.18.

These data can be treated graphically in a number of ways. W. J. Whitehouse and W. Galbraith and the author made the interesting observation that in the case of even-even nuclides, the half life for spontaneous fission seems to decrease with an exponential dependence on Z^2/A, while nuclides with an odd number of nucleons (neutrons or protons or both) decay by this process at a

TABLE 3.18 *Summary of Spontaneous Fission Half Lives*

ISOTOPE	HALF LIFE
Th^{230}	$>1.5 \times 10^{17}$ y*
Th^{232}	$\geq 10^{21}$ y
U^{232}	$8 \pm 5.5 \times 10^{13}$ y
U^{234}	1.6×10^{16} y
U^{235}	1.8×10^{17} y
U^{236}	2×10^{16} y
U^{238}	$5.9 \pm 0.4 \times 10^{15}$ y
Pu^{236}	3.5×10^{9} y
Pu^{238}	4.9×10^{10} y
Pu^{239}	5.5×10^{15} y
Pu^{240}	1.32×10^{11} y
Pu^{242}	$7.25 \pm 0.3 \times 10^{10}$ y
Pu^{244}	$2.5 \pm 0.8 \times 10^{10}$ y
Cm^{240}	1.9×10^{6} y
Cm^{242}	7.2×10^{6} y
Cm^{244}	1.4×10^{7} y
Cm^{246}	3×10^{7} y
Cm^{248}	4.6×10^{6} y
Cm^{250}	2×10^{4} y
Bk^{249}	6×10^{8} y
Cf^{246}	$2.1 \pm 0.3 \times 10^{3}$ y
Cf^{248}	7×10^{3} y
Cf^{249}	1.5×10^{9} y
Cf^{250}	$1.5 \pm 0.5 \times 10^{4}$ y
Cf^{252}	66 ± 10 y
Cf^{254}	56.2 ± 0.7 d*
E^{253}	3×10^{5} y
E^{254}	1.5×10^{5} y
Fm^{252}	>3000 d
Fm^{254}	200 d
Fm^{255}	>60 y
Fm^{256}	3 h*

* y = years; d = days; h = hours.

much slower rate. Thus a plot of the logarithm of the partial spontaneous fission half life against Z^2/A resulted in a fairly good straight line for the limited data available. With the accumulation of more data it became apparent that, although the parameter Z^2/A accounted broadly in this manner for the variation in half life over a range of Z values, for a given value of Z this parameter

did not account for the variation of half life with A. Thus J. R. Huizenga pointed out that for a given value of Z the half life goes through a maximum as A varies. In addition, there is a dramatic increase in the rate for nuclides with more than 152 neutrons as pointed out by A. Ghiorso. A plot of the logarithm of the half life versus Z^2/A is shown in Fig. 3.32. It is interesting to note that the line in Fig. 3.32 reaches the region of instantaneous rate of spontaneous fission (that is, half life of the order of 10^{-21} sec.) at a value of about 46 for Z^2/A, which is close to the various predicted limiting

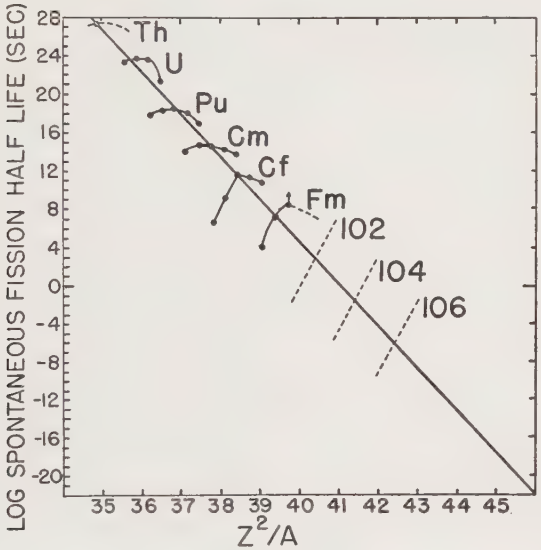


Fig. 3.32 Plot of logarithm of partial half life for spontaneous fission versus Z^2/A.

values for Z^2/A on the basis of the liquid drop model. The curves for the elements uranium through fermium have been used to predict the shape for the higher elements. Also, the average spacing between the curves for the elements plutonium through fermium has been used to establish the position of the elements above fermium.

Other correlations involving the ratio of spontaneous fission to alpha half lives have also been useful for predictive purposes. A very useful correlation, due to A. Ghiorso, is shown in Fig. 3.33, where the dramatic effect at 152 neutrons is prominently shown. Again,

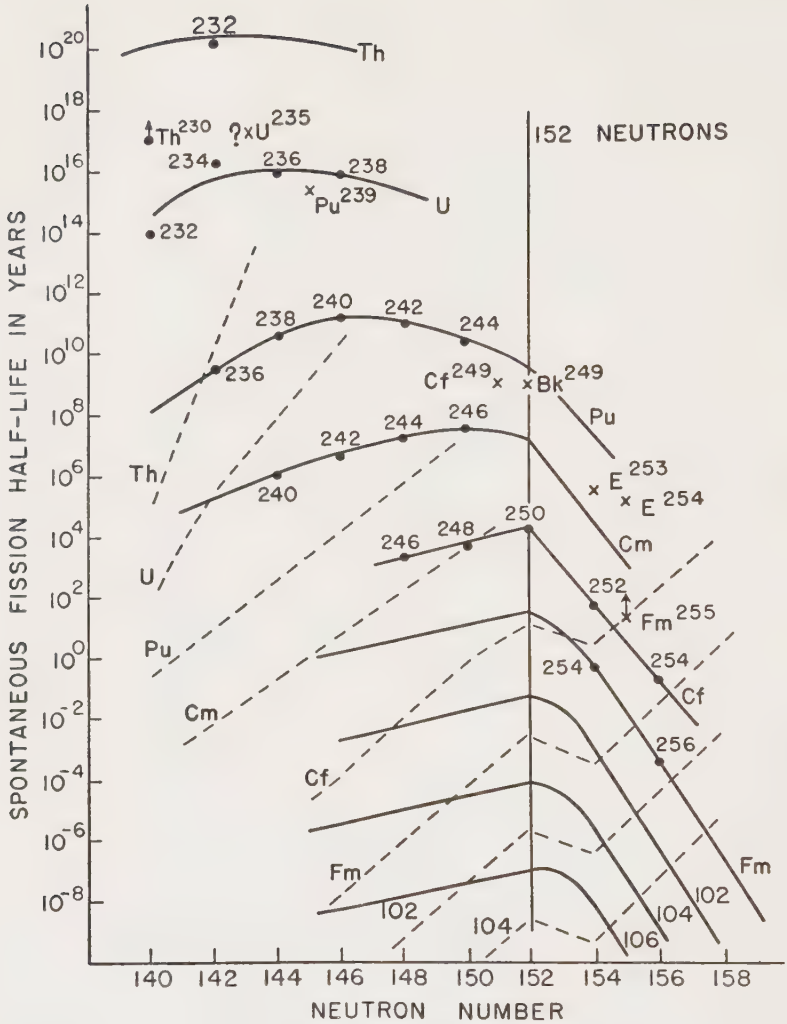


Fig. 3.33 Plot of logarithm of partial half life for spontaneous fission versus neutron number. The arrow above a point indicates that this is the lower limit to its half life. The dotted lines refer to the partial half lives for alpha decay. (Plot by A. Ghiorso.)

the spacing and shape of the lines corresponding to transfermium elements are drawn by taking into consideration the spacing and shape of the lines representing the known data for the preceding elements. The points representing the half lives for nuclides with

odd nucleons show that these are on the average 10^3 to 10^5 times longer than would correspond to even-even nuclides.

W. J. Swiatecki has made an important contribution to the understanding of spontaneous fission rates of even-even nuclei, particularly with regard to the parabolic dependence on A for a given Z and the enhanced fissionability beyond 152 neutrons. He calculates fission barrier heights by considering the energy difference between a smooth-saddle-point energy surface (as a function of Z and N) and the actual ground state masses. The lowered neutron binding energy beyond the 152 subshell is reflected in significant barrier height decreases with each added pair of neutrons beyond 152. From the success of Swiatecki's approach in the correlation of spontaneous fission rates, we must conclude that the saddle-point-energy surface is somewhat freer of the shell effects influencing the ground state energy surface, although as the distance between the two surfaces decreases with increasing Z it is expected that the shell effects in the saddle point surface will be important. The spontaneous fission rate is a very sensitive function of the difference in energy between the saddle point and the ground state surface. Thus the spontaneous fission rate of a nuclide of unknown mass can be used to determine the distance of its point on the saddle point surface above its point on the ground state surface and hence can be used to determine, with high sensitivity, its mass.

Rasmussen has called attention to a dynamic quantum effect which might also operate to enhance spontaneous fission beyond 152 neutrons. The slippages of pairs of nucleons from one orbital to another, in such a way as to minimize nucleonic energy as fission proceeds, would be enhanced by deviations of the nuclear shape away from symmetries, such as the rotational symmetry about the z' axis or reflectional symmetry about the equatorial plane as pointed out by D. L. Hill and J. A. Wheeler. He notes that the first excited gamma vibrational state ($2+$, $K = 2$) drops in Fm^{254} (beyond 152 neutrons) to a considerably lower value than the average for $N < 152$. This drop may indicate a softening of the nucleus toward gamma vibrations, which affect the axial symmetry, and consequently there may be a larger zero point amplitude for gamma vibrations in the ground state for nuclei with $N > 152$. Data are too meager to test the generality of such an effect, but the predic-

tion from the above hypothesis would be that a dropping of the energy positions of either the gamma vibrational states or the $(1-, K = 0)$ states would correlate with enhanced spontaneous fissionability.

J. O. Newton and, later, Wheeler have offered an attractive explanation for the reduced rates of spontaneous fission of odd-nucleon nuclides using the strong coupling approximation of the unified model of Bohr and Mottelson. This explanation follows from the quantization of the intrinsic angular momentum, $\Omega\hbar$, of the nucleonic system about the symmetry axis, and the fact that this intrinsic angular momentum for the state of lowest energy changes with increasing spheroidal deformation, δ, in the case of odd nuclei, whereas for even-even nuclei the nucleonic state $\Omega = 0$ lies lowest at all deformations. Thus in the case of even-even nuclei the top pair of protons or neutrons can readjust their orbits while conserving angular momentum as the energies associated with the orbital change with increasing deformation. In the case of odd nuclei a given nucleonic component of angular momentum Ω can only be maintained during the change of orbital position with increasing deformation by introducing nucleonic excitation energy into the system at the expense of kinetic energy in the fission mode. Wheeler makes a rough estimate of this excitation (which he terms *specialization energy*) using Nilsson's curves (Figs. 3.14 and 3.15) for the dependence of individual nucleon energy upon deformation. In this manner, Wheeler estimates sufficient additional activation energy for fission of odd nuclei to account on the average for the outstandingly slower spontaneous fission rates for odd nuclei.

It should be pointed out that Wheeler's estimate of the specialization energy will generally be somewhat high, since the quantum number K (or Ω) is not a strictly good quantum number. As the odd nucleus moves along its fission trajectory, it must exactly conserve parity and total angular momentum, but it is not restricted to a single K value, as Wheeler assumes. It is well known that Coriolis forces couple intrinsic states of differing K. For example, at a level crossing a spin $5/2$, $K = 5/2$, state a nucleon could "slip" into a spin $5/2$, $K = 3/2$, state. Since K must be less than or equal to I, it would seem that the specialization energy restriction would be most severe for $I = 1/2$, since K can only equal $1/2$. One

might expect low spin odd nuclei to show the greatest hindrance in spontaneous fission if it were not for the fact that there are more orbitals with $\Omega = 1/2$ than with higher values. The actual data on hindrance show no correlation with spin. Indeed, Swiatecki correlates odd-nuclei spontaneous fission rates smoothly with his mass difference approach.

It is clear that in a short account such as this, it has been only possible to give some indication of the rich mass of information and the correlation of this information which are available concerning the nuclear properties of the transuranium nuclides. It can only be hoped that I have chosen wisely and not left out too much of major importance.

Chapter 4. Future Synthetic Elements

The search for new synthetic elements, which must be heavier transuranium elements, is a continuing goal. The many facets of this problem will be examined in some detail and in a somewhat fanciful manner in this chapter. The most important considerations are the methods of detection of the new elements, the predicted chemical properties, the predicted decay properties, and the production and yields of the nuclear reactions which might be used. These will be discussed in that order. However, after a discussion of the detection methods, we shall interpose a description of the discovery of mendelevium (atomic number 101) as an illustration of some of the considerations involved.

4.1 Methods of Detection

The methods of detection of the expected heavy isotopes through measurement of the characteristics of their decay processes have reached such a great sensitivity that in favorable cases as few as one or two atoms per experiment can be detected and characterized. This high detection efficiency is available for samples which emit alpha particles or decay by spontaneous fission; fortunately, one of these modes of decay is to be expected in most cases. The weightless sample is placed on a flat plate in a gridded ionization chamber which is connected to an amplifier and pulse discrimination circuit, after which the pulse is recorded in some manner.

The high detection efficiency obtainable for alpha particles is coupled with other unique advantages. Since the range of an alpha particle is very small—less than 0.001 inch in most materials—it is possible to obtain essentially zero background (that is, any events

observed when a sample is not present) by choosing materials for chamber construction that are not alpha radioactive. External sources of other radiations will normally not interfere. Further, an isotope partially or totally decaying by alpha emission will usually radiate its alpha particles predominantly at a single energy. Thus if one has sufficient resolution, it is possible to identify an alpha particle as having been emitted by a particular isotope. This unique instrumental identification is not possible by the present means of detecting nuclear radiations from beta or electron-capture processes, since the combination of high sensitivity, zero background, and high resolution is not available.

The spontaneous-fission process, however, allows one to take advantage of the first two but not the third of these requirements, for the following reasons: (1) each atom undergoing spontaneous fission can be detected with 100 per cent efficiency, since the two fission fragments are released in exactly opposite directions; thus, if a sample is mounted on a flat plate, one of the fragments always enters the counting volume of the chamber; (2) zero backgrounds are easily obtainable, and the range is small for each fragment; (3) the energy of spontaneous fission does not differ enough from one atom to another to allow an analysis to be made on this basis, but the mere fact that it is observed allows the general conclusion that the atom probably has an even number of protons and an even number of neutrons in its nucleus before the breakup.

In parallel with the development of the nuclear detectors, there have been continuing efforts to improve the pulse-sorting techniques necessary to store the information obtained. The methods used have varied from the simplest one of merely photographing the face of an oscilloscope tube to very elaborate electronic systems stemming from the new computer industry. At the present time in our laboratory we are using a system of multiple, alpha-particle, pulse-analyzing chambers that will enable us to record simultaneously for each event the chamber in which it occurs, the time when it occurs, and its energy in terms of pulse height. Thus we are able to completely identify, chemically and physically, each atomic disintegration as it occurs. For the very short-lived isotopes special detection and recoil-catching devices at the target are required.

Detection of alpha particles in photographic emulsions also offers high sensitivity, but it is difficult to combine this with chemical identification.

4.2 Mendelevium as an Example

We shall now illustrate some of the factors involved by describing the discovery of element 101, which was in many ways the most dramatic of them all. We decided to make an attempt in a situation that would have been regarded by most sensible people as very premature. All of the other discoveries of transuranium elements had been based on starting with weighable amounts of target materials; however, it was thought that techniques had advanced to a point where it might be possible to identify element 101 as a transmutation product produced in a target of unweighable amount.

The plan of attack involved the bombardment of the maximum quantity available of einsteinium in the form of the isotope E^{253} with helium ions (40-Mev energy) in the Berkeley 60-inch cyclotron. On gathering together all of the E^{253} that was available as the result of its production in the Arco MTR reactor (according to the reactions illustrated in Fig. 3.1 above), the total quantity was found to amount to about 10^9 atoms. In order to assay the possibilities, the number of atoms of element 101 which could reasonably be expected from the bombardment could be deduced from the following simple considerations. The number of atoms, N, of element 101 should be approximately equal to:

$$N \cong N'\sigma It$$

where N' designates the number of einsteinium atoms used as a target; σ, the cross section or probability for the reaction; I, the intensity of the helium-ion beam; and t, the effective time of the bombardment. Since the cross section, σ, could be predicted to be about 10^{-27} square centimeters on the basis of the known values for previously observed, similar reactions in this region, we have all the data needed to make the estimate. As the result of certain fundamental changes in the cyclotron, made to increase the intensity of the helium-ion beam to a value higher than ever before attained,

it was possible to attain 100 microamperes or about 10^{14} particles per second per square centimeter for I. Predictions for the average life of the expected isotopes suggested the range of hours, so that an effective value of t of the order of 10^4 seconds was all that could be utilized. Using these numbers, the calculations could be made as follows:

$$N \cong 10^9 \times 10^{-27} \times 10^{14} \times 10^4 \cong 1 \text{ atom}$$

Thus realistic considerations corresponding to the most optimum conditions indicated that we could expect no more than *about one atom of element 101 per experiment!*

Adding immeasurably to the complexity of the experiment was the absolute necessity for the chemical separation of the one atom of element 101 from the 10^9 atoms of einsteinium in the target and its ultimate complete chemical identification by separation in the eka-thulium position in the now familiar ion-exchange method. This separation and identification would presumably have to take place in a period of hours, or even one hour or less, because the expected half life was of this order of magnitude.

These requirements indicated the desperate need for new techniques, together with some luck, and, fortunately, both were forthcoming. The new technique involved the separation of element 101 by the recoil method from the einsteinium in the target. The einsteinium was placed on a gold foil in an invisibly thin layer. The helium-ion beam was sent through the back of the foil so that the atoms of element 101, recoiling because of the momentum of the impinging helium ions, could be caught on a second thin gold foil. This second gold foil, which contained recoil atoms and was relatively free of the einsteinium target material, was dissolved, and the chemical operations were performed, beginning with this solution.

The earliest experiments were confined to looking for short-lived, alpha-emitting isotopes that might be due to element 101. For this purpose it was sufficient to look quickly in the actinide chemical fraction as separated by the ion-exchange method. No alpha activity was observed that could be attributed to element 101, even when the time between the end of bombardment and the beginning of the alpha-particle analysis had been reduced to five minutes.

However, the experiments were continued, and in one of the subsequent bombardments a single large pulse due to spontaneous fission was observed. With probably unjustified self-confidence, it was thought that this might be a significant result. Although such an attitude might ordinarily have been considered foolish, it must be recalled that rapid decay by spontaneous fission was up until that time confined to only a few isotopes, none of which should have been introduced spuriously into the experiment or produced in the experiment. In addition, background counts caused by this mode of decay should be essentially zero in proper equipment.

The major question, of course, was whether the experiment could be repeated. In a number of subsequent bombardments, a spontaneous fission event or two were observed in some, while none were observed in others. This, of course, was to be expected, because of the statistical fluctuations inherent in the production of the order of one atom per bombardment. Furthermore, preliminary chemical experiments seemed to indicate that the spontaneous fission counts, when they did appear, came in about the element 100 or 101 chemical fractions. At about this time a huge fire bell was hung in the hall of the chemistry building, connected to the counting circuit in such a manner that a loud clang rang out on each occasion when one of these rare spontaneous fission events registered. This sport was put to a justifiable end when it came to the attention of the fire department.

The definitive experiments were performed in a memorable all-night session, February 18–19, 1955. Three successive three-hour bombardments were made, and, in turn, their transmutation products were completely and quickly separated by the ion-exchange method, using Dowex-50 resin (a sulfonated polystyrene) at 87°C with alpha-hydroxyisobutyrate elution. Some of the isotope E^{253} was added in each case, so that together with the Cf^{246} produced from Cm^{244}, also present in the target, it was possible to define the positions in which the elements came off the column. Five spontaneous-fission counters were then used to count simultaneously the corresponding drops of solution from the three runs. A total of five spontaneous-fission counts were observed in the element 101 elution position, while a total of eight spontaneous-fission counts were also observed in the element 100 position, and no such counts were

observed in any other position. The original elution data are presented in Fig. 4.1, and a picture of the original stylus tracing from the spontaneous-fission recording system is shown in Fig. 4.2.

It is interesting to note that the chemical behavior of one or two atoms could faithfully reflect the chemical behavior of the new element. This is apparently due to the fact that the same atom went through the same chemical reactions (adsorption and elution) hun-

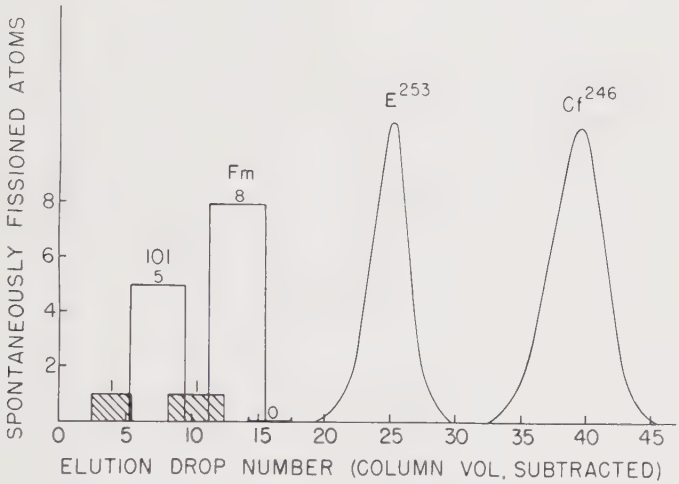


Fig. 4.1 Original elution data corresponding to discovery of mendelevium (Feb. 19, 1955). (Dowex-50 resin at 87°C with alpha-hydroxyisobutyrate elution.) The curves for E^{253} and Cf^{246} represent alpha radioactivity.

dreds of times during its travel down the ion-exchange column, giving a substantial statistical sample of its behavior.

The spontaneous-fission activity in both the element 101 and 100 fractions decayed with a half life of about three hours. This and other evidence has led to the hypothesis that the mendelevium isotope has the mass number 256 and decays by electron capture with a half life of the order of a half hour to the isotope Fm^{256}, which is responsible for the spontaneous-fission decay.

On the basis of this evidence, the group, consisting of A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and the author, announced to the world the discovery of element 101. The name mendelevium was suggested in recognition of the pioneering role

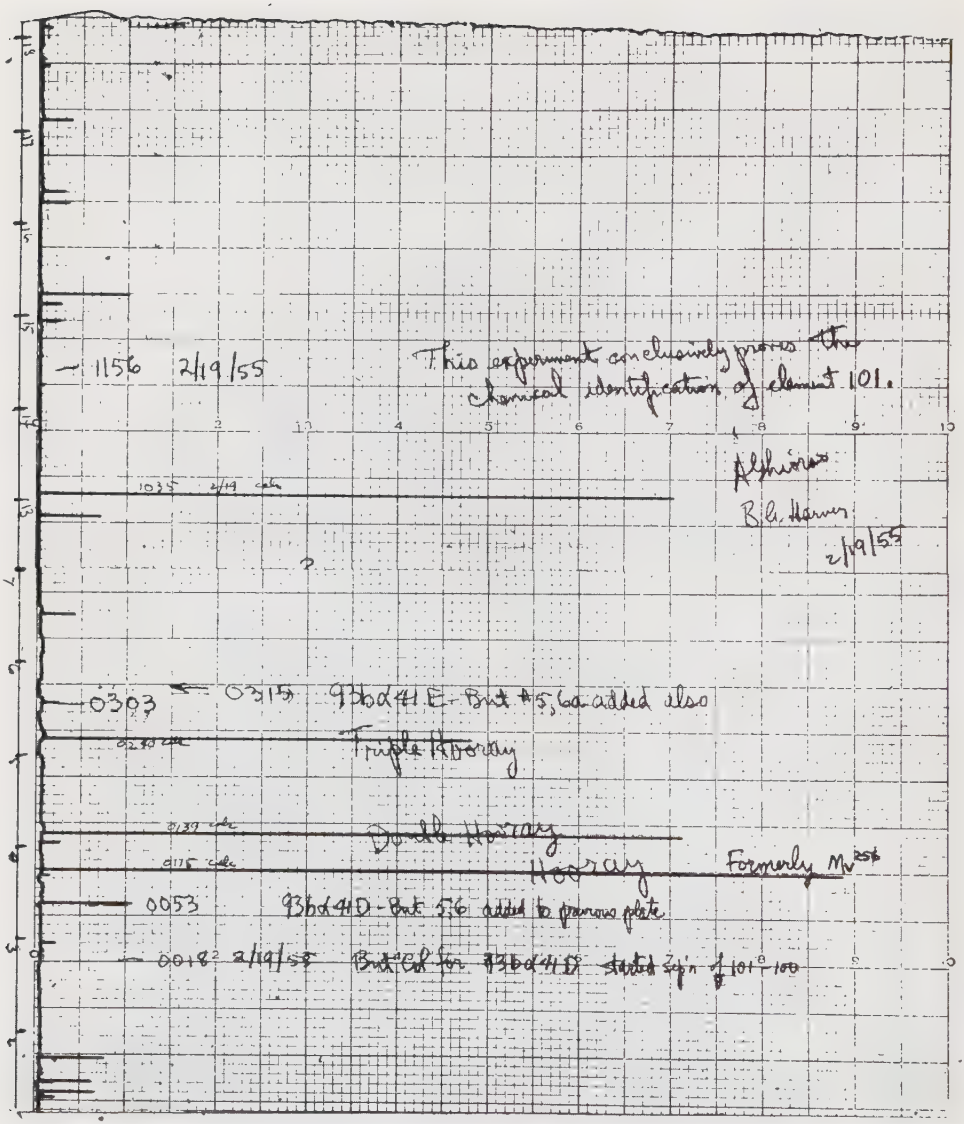


Fig. 4.2 Reproduction of original data sheet showing stylus tracing (and various annotations) from a spontaneous-fission recording system, corresponding to discovery of mendelevium (Feb. 19, 1955)

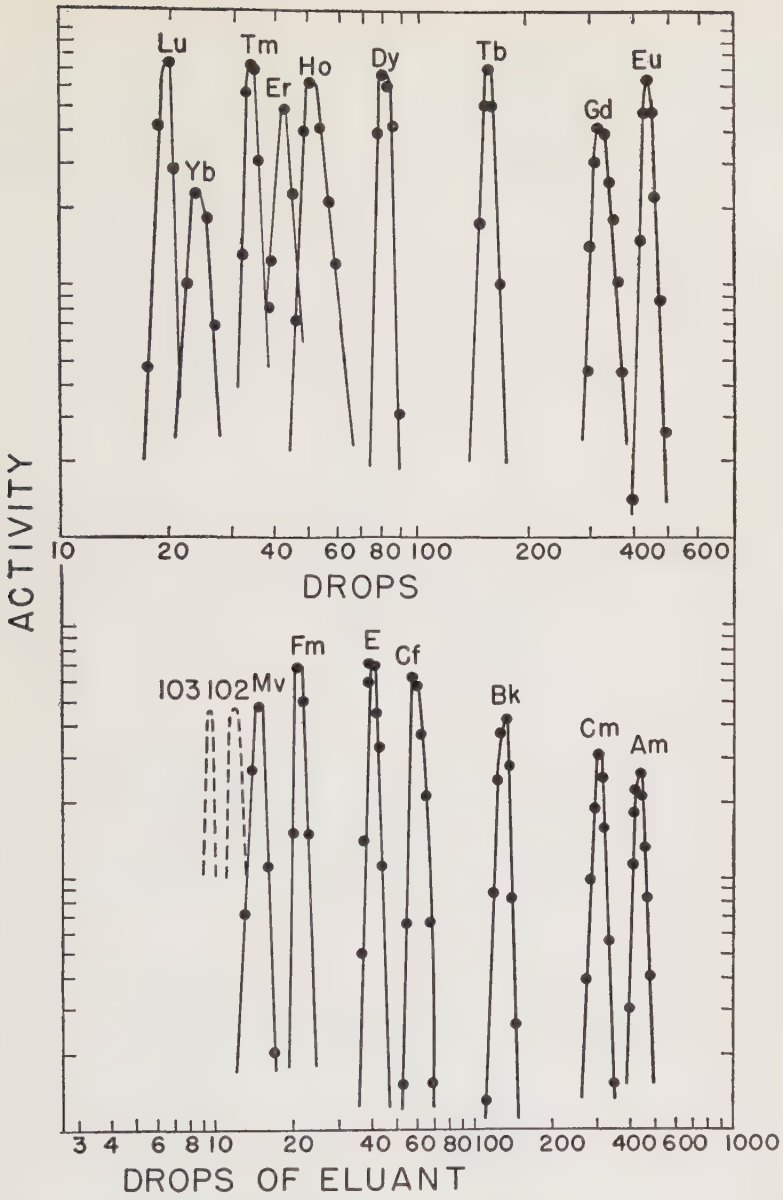


Fig. 4.3 Elution of homologous actinides and lanthanides from Dowex-50 at 87°C with alpha-hydroxyisobutyrate as eluant. (Complete elution curve for mendelevium is traced for first time.)

of the great Russian chemist, Dmitri Mendeleev, who was the first to use the periodic system of the elements to predict the chemical properties of undiscovered elements, a principle which has been the key to the discovery of the last seven transuranium elements. It is comforting to be able to record the fact that subsequent experiments by the same group using larger amounts of einsteinium in the target have led to the production of over one hundred atoms of mendelevium, lending confirmation to the somewhat tenuous original conclusion. Again the Dowex-50 resin was used with the eluting agent alpha-hydroxyisobutyrate at a temperature of 87°C.

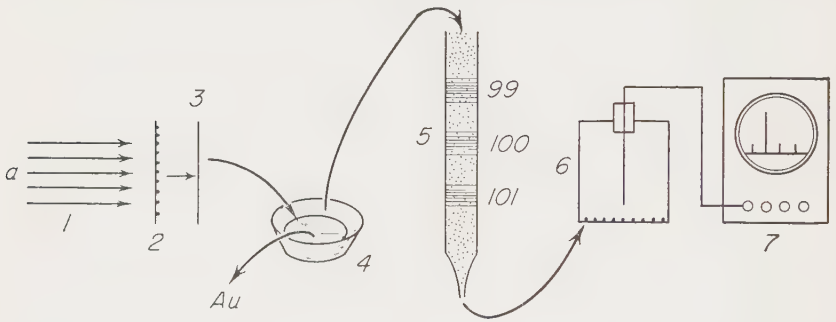


Fig. 4.4 Reproduction from the Russian journal *Priroda* illustrating graphically the major steps in the mendelevium discovery experiment. (1) Helium ion beam, (2) Target foil with E^{253} on back side, (3) Gold foil to catch recoil (Mv^{256}) atoms, (4) Chemical separation apparatus to separate actinides from the gold foil, (5) Ion exchange column to separate actinides from each other and identify elution position of mendelevium, (6) Spontaneous-fission chamber, (7) Electronic device to record spontaneous-fission pulses.

Fig. 4.3 shows these data together with elution data taken under the same conditions for the other tripositive actinides, fermium to americium, inclusive, and the corresponding tripositive lanthanides. Included are the predicted elution positions for elements 102 and 103, which are probably the most accurate of these predictions and will, therefore, be referred to in the following section where the chemical properties of transmendelevium elements are estimated. It should be noticed that Fig. 4.3 is a log-log plot, which is convenient because of the large spread of elution volumes represented therein. The indications are that mendelevium is a typical tripositive actinide element and a true eka-thulium, as expected.

An interesting review of the mendelevium experiment was published in the Russian journal *Priroda*, from which one of the illustrations is reproduced as Fig. 4.4; this summarizes all of the steps in graphic form.

Thus it can be seen that in the search for new elements a preliminary separation from the target material can be effected through the use of the recoil technique. This will certainly be utilized, especially in the cases where small amounts of target material are available for the experiment. The technique may be generally necessary because of the short half lives to be expected, as will be discussed below.

4.3 Prediction of Chemical Properties

We shall begin the discussion of the predicted chemical properties by referring to the periodic table (Fig. 2.1, above) and to some of the considerations given in Chapter 2. Thus we see that element 103, eka-lutetium, should complete the actinide transition series of elements. It is expected that elements 104, 105, 106, and so on, will be fitted into the periodic table under hafnium, tantalum, tungsten, and so on. The electronic structures of some transactinide elements are given in Table 4.1. The electronic $6d$ shell should

Table 4.1 *Predicted Electronic Structures of Some Transactinide Elements*

Element	Electronic structure (beyond radon)
104	$5f^{14}6d^{2}7s^{2}$
105	$5f^{14}6d^{3}7s^{2}$
106	$5f^{14}6d^{4}7s^{2}$
107	$5f^{14}6d^{5}7s^{2}$
108	$5f^{14}6d^{6}7s^{2}$
112	$5f^{14}6d^{10}7s^{2}$
113	$5f^{14}6d^{10}7s^{2}7p^{1}$
118	$5f^{14}6d^{10}7s^{2}7p^{6}$

undergo filling with these elements, which may be designated as eka-hafnium, eka-tantalum, eka-tungsten, and so on. It might be added, mainly for the sake of completeness, that the filling of the

6*d* shell should be followed by the addition of electrons to the 7*p* shell, with the attainment of the rare-gas structure at hypothetical element 118. (The degree to which this may be a typical "rare gas" is open to some question, because of the possible advent of the 5*g* shell filling near this point, but this need not concern us here.) Thus it can be seen that the position in the periodic table of the elements all the way up to hypothetical element 118 can be predicted as a consequence of having determined the point of filling of the 5*f* shell (element 103), and therefore the chemical properties of all of these elements can be estimated to the extent that the membership of an ordinary element in a certain group in the periodic table foretells the chemical properties of that group. Of course, as the considerations below will show, there is probably no prospect that elements with atomic numbers as high as some of those mentioned here will ever be found.

It seems certain that the chemical identification of elements 102 and 103 will be made through the use of the ion-exchange adsorption and elution method described in Chapter 2 and illustrated in Section 4.2 above. Some predicted elution positions, for the ion exchange resin Dowex-50 and elution with alpha-hydroxyisobutyrate ion at 87°C, are shown in Fig. 4.3. Here, again, the elution positions of the lanthanide elements are shown for comparison and aid in the prediction. The elution position of the mendelevium was determined in an experiment, referred to above, in which somewhat over a hundred atoms were produced. Element 102 might be expected to have, in addition to a stable III oxidation state, a somewhat unstable II oxidation state in aqueous solution, because of the special stability of the $5f^{14}$ electronic configuration and by analogy to the II state of ytterbium. The II oxidation state of element 102 may very well play an important role in its chemical identification. If the stability of this state is comparable to the stability of the II state of ytterbium, then a rapid separation of this element from other actinide elements may be effected through electrolytic or amalgam reduction, using ytterbium as a carrier. The stability of the II state may be reflected in the properties of the metal, which may utilize only two bonding electrons per atom, leading to an unusually low density (ca. 8) and relatively high volatility for element 102. Both the metal and the II state of element 102 will be

non-magnetic (diamagnetic). Mendelevium might have an even more unstable II oxidation state for similar reasons. Element 103 should have only the III oxidation state. The tracer quantities of these elements will be coprecipitated with the usual lanthanide carriers and generally resemble the lanthanide elements in their chemical properties. Their ions should generally form stronger anion complexes than the lanthanide ions, and, in fact, these should also in general be the strongest of those in the actinide group.

The chemical properties of element 104 can best be estimated by considering those of titanium, zirconium, and hafnium as well as those of cerium (IV), terbium (IV), and thorium (IV). Crystal structure data are relevant in this connection, and some pertinent ionic radii are summarized in Table 4.2 (including a predicted

TABLE 4.2 *Ionic Radii of Some Tetrapositive and Tripositive Elements*

Ti	0.60 Å	Sc	0.68 Å
Zr	0.77	Y	0.90
Ce	0.92	La	1.06
Tb	0.84	Gd	0.94
Hf	0.77	Lu	0.85
Th	0.99	Ac	1.11
104	(0.77)	Cm	0.98
		103	(0.88)

(predicted values are given in parentheses)

value for element 104) together with some values for tripositive elements (including a predicted value for element 103) for comparison. Each of these columns of values corresponds, insofar as possible, to analogous compounds within each of the two groups. It will be noticed that the values for the ionic radii decrease in going across the lanthanide group (lanthanum 1.06, gadolinium 0.94, lutetium 0.85). This is due to the well-known "lanthanide contraction" (discussed in Chapter 2) which results from the fact that the successive electrons are added to the inner 4*f* shell, leading generally to identical molecular structures for analogous compounds; the increasing nuclear charge in going across the group then results in the decreasing size of the ions. This leads to a corresponding decrease in the degree of electropositive character of the elements

in the series, so that lutetium is less electropositive than gadolinium, which, in turn, is less electropositive than lanthanum. Similarly, the order with the actinides is element 103 (predicted) less than curium, which, in turn, has less such character than actinium. Another consequence is that the heaviest lanthanides generally form the strongest complexes in the group, and the heaviest actinides should form the strongest complexes in the actinide group. (More specific chemical considerations come in to account for the fact that the actinides often form stronger complexes than the lanthanides as discussed in Chapter 2.)

Thus it can be seen that element 104 (and following elements) will have small ionic (and covalent) radii and be less electropositive than might possibly have been expected at first glance. Element 104 should be exclusively tetrapositive in aqueous solution, leading to somewhat simple chemical properties. Element 104 may be expected to form di- and trihalides only under the most extreme reducing conditions, as may be deduced by an extrapolation of the trend of decreasing stability of lower halides in going from zirconium to hafnium; thus the lower halides of element 104 may well be more unstable than those of thorium. In the metallic state of element 104 there will be a marked increase in density and a sharp drop in volatility as compared with the metallic state of the immediately preceding element 103, owing to the rise in the number of bonding electrons from three to four.

Zirconium should be an adequate carrier, and a number of compounds which are insoluble in acid solution, such as the iodate, mandelate, etc., should be suitable for this purpose. The fluoride of element 104 should be soluble, like those of hafnium and zirconium and unlike those of cerium (IV) and thorium. Thus a separation from the actinide elements might be effected under proper conditions, by precipitating the insoluble fluorides of the tripositive actinides, leaving element 104 in solution.

However, the specificity of such procedures might not be so great as one would like to have for the identification of the atomic number, and for this we might again want to turn to an ion exchange, adsorption-elution system. The possibilities are legion, and we shall merely illustrate with an example or two. A sequence involving tracer zirconium and hafnium has attractive possibilities.

However, since the predicted ionic radius of element 104 is identical with those of zirconium and hafnium, it is difficult to predict the elution order, insofar as it depends on this somewhat doubtful criterion. A possibility, using the cation-exchange resin Dowex-50 and 6 *M* hydrochloric acid as the eluting agent and assuming retention of the elution order according to the inverse order of the atomic numbers, is shown in Fig. 4.5. Similarly designed methods depend-

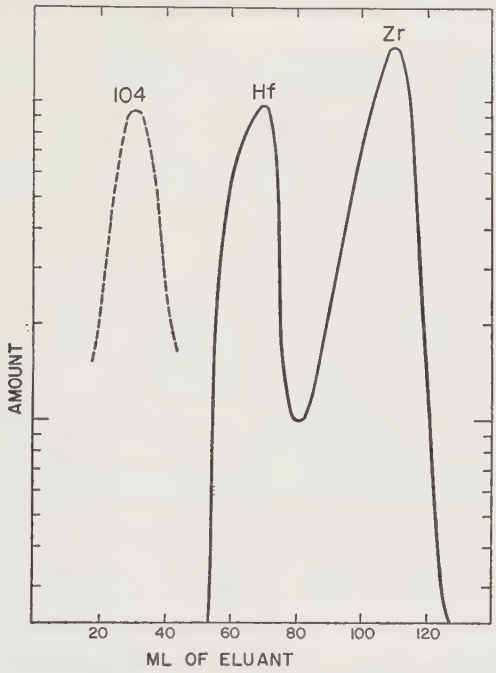


Fig. 4.5 Elution of hafnium and zirconium from Dowex-50 resin with 6 *M* hydrochloric acid at room temperature, showing predicted elution position for element 104. (Data for hafnium and zirconium from K. Street, Jr., and the author.)

ing on extraction into organic solvents might also be effective and could have the advantage of being potentially faster, which will be a matter of great importance. Another possibility would be the use of an anion system, again in conjunction with tracer zirconium and hafnium involving 0.2 *M* hydrochloric acid, 0.01 *M* hydrofluoric acid, and the anion exchange resin Amberlite IRA-400 (a quaternary ammonium polystyrene); this system has the advantage that the III state actinides are not adsorbed.

Solvent extraction may prove to be a rapid and effective method of separating element 104 from the heavier actinide elements. For example, ratios of distribution coefficients under comparable conditions for typical IV and III ions in the acidified water—TTA–benzene system range from 10^{10} to 10^{5}. The ratio for Hf^{+4}/Lu^{+3}, which is approximately 10^{10}, is probably the most pertinent for an estimation of the expected element 104–heavy actinide separation. Similar excellent separations between IV and III ions are found for the system, acidic aqueous solution—TBP (tributyl phosphate)–hydrocarbon solvent, where again the element 104 in the IV state should be extracted into the organic solvent to a much greater extent than is the case for the tripositive ions. Many other organic complexing agents, such as various β-diketones, ethylenediaminetetraacetic acid (EDTA), cupferron, etc., likewise offer the possibility of good separation.

This seems like a good place to emphasize that element 104 may not have any isotopes with half lives sufficiently long to allow application of procedures such as are proposed here. This will be discussed in some detail below. It may be necessary to use much simpler and faster identification methods, involving volatility, migration, reactions with surfaces, or gas flow reactions, etc., to make some semblance of a chemical identification. This is even a greater possibility for the heavier elements to be discussed next. However, it is interesting to make such predictions, if only for their own sake, and this will be regarded as sufficient justification for doing so.

Element 105 should resemble niobium and tantalum (and to some extent protactinium), with the V oxidation state expected to be the most important state. This suggests rather troublesome chemical properties, with hydrolysis and the formation of colloids and polymers playing important, if not dominant, roles. In order to hold it in acidic solution under ordinary conditions it will be necessary to form complex ions, for example, with ions like the fluoride ion. Tantalum should be a good carrier, but unfortunately the common methods of precipitating tantalum from aqueous solution, such as by hydrolysis, would not be very specific for element 105. Although it is not a true chemical homologue of protactinium, element 105 might resemble protactinium in carrying properties to some extent. Thus it might be carried by precipitates which carry

protactinium, such as zirconium iodate, manganese dioxide, etc., and might be extracted into organic solvents which extract protactinium, such as diisopropyl ketone. By comparison with the ionic radii of niobium (V) (0.70 Å) and tantalum (V) (0.73 Å), an ionic radius of approximately 0.76 Å might be expected for element 105 (V).

An example of an ion exchange method for the identification of the atomic number of element 105, in conjunction with tracer niobium and tantalum, might be the use of the anion exchange resin Dowex-1 (a quaternary ammonium polystyrene), with a mixture of hydrochloric and hydrofluoric acids as eluant. Niobium would elute first, followed by tantalum, with a 9 *M* hydrochloric acid–0.05 *M* hydrofluoric acid mixture; then if the sequence is pre-

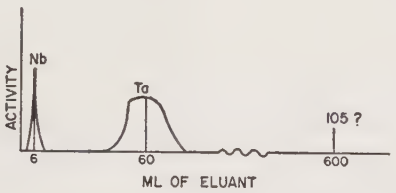


Fig. 4.6 Elution of niobium and tantalum from Dowex-1 resin with 9 *M* hydrochloric acid – 0.05 *M* hydrofluoric acid at room temperature, showing predicted elution position for element 105. (Data for niobium and tantalum from K. A. Kraus and G. E. Moore.)

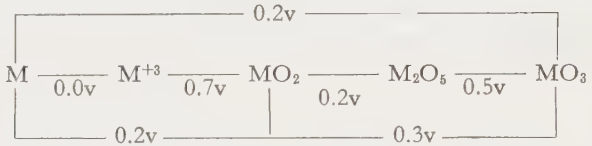
served it might be necessary to change to a higher concentration of hydrofluoric acid (or even to use ammonium fluoride) to elute the element 105. This method has the advantage that the III state actinides are not adsorbed by the resin. This possibility is illustrated in Fig. 4.6.

Tantalum can be extracted by ketones, in a rather specific manner, from aqueous solutions containing hydrofluoric acid at a concentration of a few tenths normal together with sulfuric or hydrochloric acid at a concentration of a few normal. Element 105 might have similar extraction properties which could be estimated in some detail by an extrapolation of the trend in these solvent extraction properties between niobium and tantalum.

Ions of element 105 having oxidation states lower than V will be paramagnetic, of course, but unlike most of the paramagnetic

actinide ions in aqueous solution or in solids these will have susceptibilities given approximately by the "spin only" formula. In fact, this will be generally true of such paramagnetic ions of elements 104–114 as can be prepared. The metallic state of element 105 will be even more dense than that of 104 and still less volatile.

The chemical properties of element 106 should be deduced from an extrapolation of the chemical properties of tungsten and molybdenum (and to a smaller extent those of chromium). Thus we might expect the III, IV, V, and VI oxidation states, with an oxidation-reduction potential scheme in acid solution somewhat as follows (on the basis of $1/2\ H_2 \rightarrow H^+$ equal 0.00 volts):



The ion of oxidation state (IV) might be expected to have about the same ionic radius as tungsten and molybdenum (0.68 Å), and the IV and V states should form strong complexes with anions like cyanide, chloride, and thiocyanate ions. The VI state should be amphoteric, forming anions like MO_4^{--}, and the cation should form complex ions with anions like oxalate and halide ions. The MF_6 should be stable and boil at about 5°C (since tungsten hexafluoride boils at 19.5°C and molybdenum hexafluoride at 35°C), and it should be possible to form volatile $M(CO)_6$. An example of an elution experiment, in conjunction with tracer molybdenum and tungsten, for atomic-number identification purposes, might involve the use of the anion exchange resin Dowex-1 and the eluant 9 *M* hydrochloric acid–1 *M* hydrofluoric acid, for which the expected elution order might be molybdenum-tungsten-106. Another possibility might be the use of an inorganic anion exchanger such as hydrous zirconium oxide treated with hydrochloric acid, a system which has been suggested by K. A. Kraus; element 106 might be eluted with ammonium or sodium hydroxide under conditions where all the elements with atomic numbers 89 to 105 inclusive would remain on the anion exchanger.

Although it seems nearly certain that the ordinary chemical properties of elements 107 and 108 will be studied only with ex-

treme difficulty, if at all, it is interesting to speculate that 107 should have the ion MO_4^-, like rhenium, and be separable by anion-exchange techniques, and element 108 should have a useful volatile tetroxide like osmium.

It is interesting to note that beginning with element 107, eka-rhenium, the transuranium elements begin to have the chemical properties which were associated with element 93 and the following elements some twenty years ago, before the actual discovery of the transuranium elements. Thus elements 107, 108, 109, 110, etc. should follow rhenium, osmium, iridium, platinum, etc. in analytical chemistry schemes for the separation of the elements. In particular, the sulfides of these elements should be insoluble in acid solution. Element 106 should follow tungsten in such separation procedures to a much greater extent than is the case for uranium.

The absorption spectra of the colored ions of the *6d* transition elements will, in general, consist only of broad peaks, rather than narrow bands, as in the actinides, and probably most of the spectra will be quite sensitive to the nature of the environment—that is, aqueous solution, solid crystal, etc.

4.4 Prediction of Decay Properties

Next we shall go on to the prediction of decay properties for the future synthetic elements. A convenient starting point is to consider which nuclides in this new region will be stable toward beta decay, that is, be beta stable. The beta-stable nuclides will decay by either alpha particle emission or by spontaneous fission, and this area of nuclides is analogous to the region of stable nuclides lower in the periodic table. These are probably not the nuclides which are longest lived and which will be synthesized first, but they give us a sort of anchor point of orientation for this future region of exploration. The mass numbers of these nuclides could in principle be estimated with the aid of the closed-decay cycles of the type discussed in Chapter 3, where such predictions for elements 93 to 104 were listed in Table 3.3. However they are based more simply on the assumption that the regularities which prevail up to this region continue in this new region. The beta-stable isotopes predicted in this manner for elements 100 to 106 inclusive are shown in Fig. 4.7.

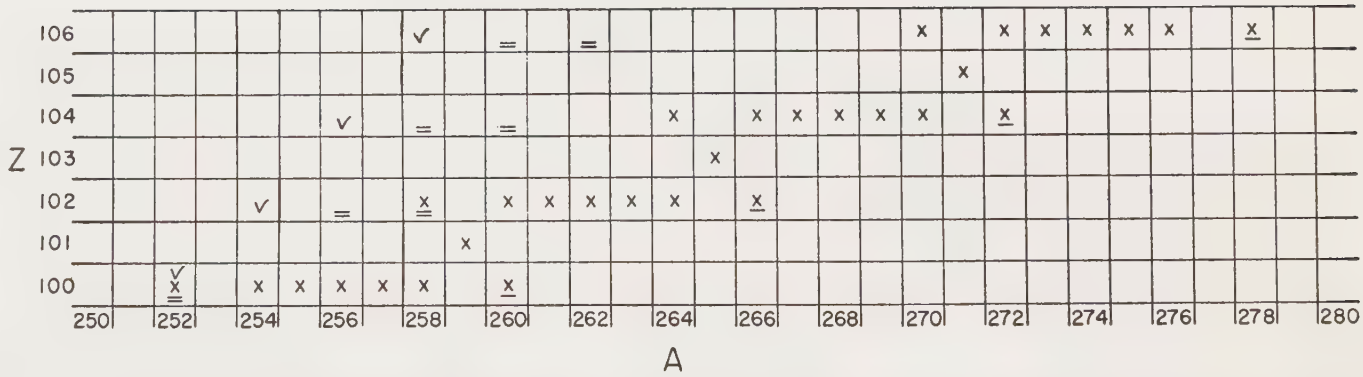


Fig. 4.7 Predicted beta-stable isotopes and longest-lived even-even nuclides (*x* indicates beta stable; $\underline{x}$, longest-lived toward alpha emission; √, longest-lived toward spontaneous fission; $\underline{\underline{x}}$ or =, longest over-all half life).

Since the alpha-decay energy decreases for a given Z with increasing A, as pointed out in Chapter 3 (see Fig. 3.12), the longest-lived beta-stable even-even alpha emitters should be 100^{260}, 102^{266}, 104^{272}, and 106^{278}, which are underlined in Fig. 4.7. However, these nuclides should have the highest spontaneous fission rates among the beta-stable nuclides if the trends in the region just below, as discussed in Section 3.9b, continue to prevail. The longest partial half lives toward spontaneous fission should be found in the nuclides with about 152 neutrons, which are indicated with a check sign ($\surd$) in Fig. 4.7; perhaps as Z increases, the effect of 152 neutrons will be felt less, and the longest partial lives for this process will move up in A, for a given Z, toward the region of beta stability. Thus the mass number of the nuclide with the longest over-all half life for each Z, neglecting beta decay which will usually not be rate-determining for the over-all decay, will be determined by these dependences of the alpha-decay and spontaneous-fission rates, which are related to A in almost opposite senses. The even-even nuclides which are predicted to have the longest over-all half lives for each Z by such rough considerations are 102^{256} or 102^{258}, 104^{258} or 104^{260}, and 106^{260} or 106^{262}. These nuclides are indicated by a double underline in Fig. 4.7. These rough predictions are made through the use of the curves in Fig. 3.12 and Fig. 3.16 from Chapter 3 for alpha decay, and Fig. 3.33 for spontaneous fission, and indicate half lives of the order of minutes for the indicated isotopes of element 102, seconds for element 104, and hundredths of seconds for element 106.

Fortunately, the nuclides with odd nucleons decay more slowly for both the alpha-emission and spontaneous-fission processes. The hindrance factors for alpha decay or retardation factors (for decay by spontaneous fission) cannot be estimated with any accuracy and, therefore, it is even more difficult to make predictions for such nuclides. A possible method of proceeding, of doubtful validity, is to use values obtained from proper averaging of all the known hindrance or retardation factors. For alpha emitters it seems best to use an "effective hindrance factor," defined as the ratio of the measured over-all alpha half life for the isotope to that expected for an even-even alpha emitter with the same ground-state transition energy and atomic number. (This differs from the usual hin-

drance factor which is defined for each individual alpha group.) The applicable effective hindrance or retardation factor might be determined by taking the geometric mean of the known effective hindrance or retardation factors for each nuclear type.

Using such methods, mean effective alpha hindrance factors of 5 for odd-even and 10 for even-odd and odd-odd nuclides are obtained. The retardation factors for spontaneous-fission decay are 10^3 to 10^4 for odd-mass nuclides and 10^5 to 10^6 for odd-odd nuclides. Thus even-odd nuclides which are predicted to have the longest half lives are 102^{257} or 102^{259}, with half lives as long as hours, and 104^{259} or 104^{261}, with half lives of the order of seconds to minutes, and 106^{261} or 106^{263}, with half lives of the order of tenths of seconds or longer. In the case of elements 103 and 105, a nuclide like 103^{260}, 103^{261}, or 103^{262} might have a half life of the order of minutes to hours, and the nuclides 105^{257} to 105^{264} might have half lives of the order of seconds or longer. *It should be emphasized that any of the nuclides mentioned, as well as others, can have a specially hindered decay, leading to a longer half life than that suggested. However there are some recent indications that the alpha-decay energies are higher and therefore the alpha half-lives are even shorter than indicated here and the effect of 152 neutrons on spontaneous fission is less than indicated here, so that the longest-lived isotopes have larger mass numbers than indicated here.*

Wheeler has made some interesting predictions concerning "superheavy nuclei." He is able to show that, if such nuclei exist, the extranuclear electrons for atoms with atomic numbers even substantially higher than 137 (often considered to be an upper limit) would behave normally because of the finite extension of the nucleus; thus there is no limitation on the existence of such heavy elements from the standpoint of the electronic structure of such atoms. By making extrapolations of a semi-empirical mass equation and assuming the applicability of the liquid drop model of the nucleus as applied to the explanation of the fission process, while neglecting all variations from nucleus to nucleus due to shell effects and other particularities, he points to the possible existence of nuclei with Z as high as 147 and corresponding A (with an excess of neutrons) of about 500. The limiting nuclei have as large an excess as possible of neutrons in order that they might survive fission, with half lives of the order of 10^{-4} seconds, and they have to be

produced at extremely high neutron fluxes (of the order of 10^{31} neutrons per square centimeter per second) such as may be available in stars. Besides the difficulties inherent in so great an extrapolation of a mass equation, Wheeler's considerations suffer from the difficulty that the spontaneous-fission rates eventually increase with A for a given value of Z (as described in Section 3.9b above), contrary to the predictions which follow from the simple liquid drop model, and hence it should not be possible to overcome the loss by fission by considering nuclei with large neutron excesses *if the known trends continue into this heavy region*. However, if the effects of closed shells on the rate of spontaneous fission are localized, there may be some regions where the predictions on the basis of the simple liquid drop model are sufficiently valid to make it possible to enter the region of higher Z values further than indicated by the simple extrapolation of the measured half lives. In any case, neutron irradiation at such extremely high fluxes would certainly lead to a greater penetration into the region of superheavy nuclei than would otherwise be possible, and any opportunity to observe the results would be very interesting. Of especial interest is the possibility of regions of special stability at closed shells; in particular there are the closed shells at 126 protons and at 184 neutrons.

4.5 Methods for Production

When we come to consider methods for the production of such new synthetic elements, we find that there will be equally difficult problems to face.

One possibility that must certainly be considered is whether the process of multiple neutron capture as the result of intense slow neutron bombardment (with the sources available on earth) over long periods of time can be used to enter the transfermium region. The prediction as to the path which such a method would take is quite straightforward, as shown in Fig. 4.8. Unfortunately, this method seems to hold little promise, because some of the intermediate isotopes which must capture neutrons have half lives so short as to preclude their presence in appreciable concentrations as required. For example, it may be predicted that Fm^{258} will decay by the spontaneous-fission process with a half life of the order of a

minute. Thus this method of production should not become important until higher neutron fluxes, say of the order of 10^{15} to 10^{16} neutrons per square centimeter per second, become available in reactors. The use of extremely high fluxes of fast neutrons from devices such as thermonuclear weapons (as described in Section 3.1a, above) or other sources which may eventually be devised (on earth) would open the paths through the neutron excess region and hence extend the possibilities.

The bombardment with deuterons or helium ions, which have been used so successfully on previous occasions, does not seem to

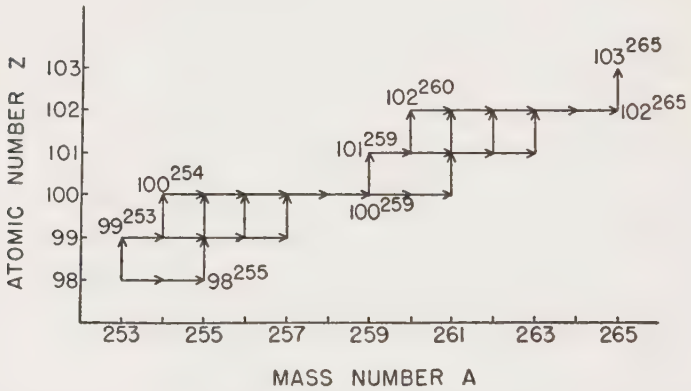


Fig. 4.8 Nuclear reaction sequences for possible production of transcalifornium nuclides by intense slow neutron irradiation. The neutron-capture reactions are interspersed with beta decays.

offer any more encouragement. The half lives of the fermium isotopes are so short that it would be difficult to build up a sufficient quantity of target material, and the situation is even worse for the use of transfermium isotopes as target material. However, the eventual production of isotopes of element 102 by the bombardment of fermium isotopes with large beams of helium ions is a definite possibility.

Fortunately, there is a type of nuclear reaction that does seem to offer more immediate hope for the production of elements with higher atomic numbers than those now known. This is the method of bombardment with heavy ions—that is, ions heavier than those of helium. A number of interesting reactions of this type have al-

ready been observed. Isotopes of californium, einsteinium, and fermium, have been produced by the bombardment of uranium with carbon, nitrogen, and oxygen ions, respectively. Such heavy ions have been accelerated in cyclotrons of the conventional design, and experiments using them have taken place in many laboratories throughout the world, including the Nobel Institute for Physics in Stockholm, the University of Birmingham, the University of California at Berkeley, and in the USSR. Two universities, the University of California and Yale University, have constructed, with funds furnished by the Atomic Energy Commission, linear accelerators which will be devoted exclusively to the acceleration of heavy ions to energies (10 Mev per nucleon) which are sufficient

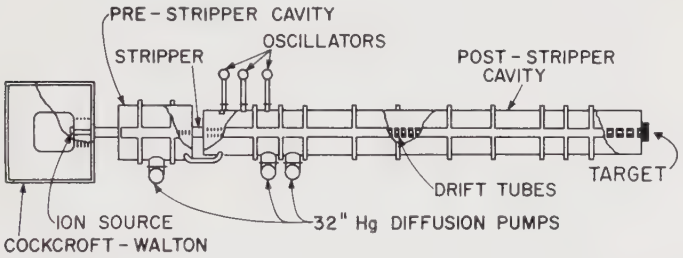


Fig. 4.9 Line drawing of University of California Heavy Ion Linear Accelerator (Hilac).

to allow them to transmute the heaviest nuclei. These machines are designed to produce rather substantial beams of all the heavy ions up to neon and have the possibility of producing usable beams of ions as heavy as argon, although the expected intensities decrease with the increasing weight of the accelerated ions. Fig. 4.9 shows a line drawing which illustrates the principles under which these machines operate, while Fig. 4.10 shows a picture of the Berkeley machine.

However, in bombardments of this type also the overwhelming proportion of the over-all reaction cross section corresponds to the fission reaction. The proportion that goes into any particular applicable spallation reaction appears to be of the order of a few parts per million or less of the total reaction cross section, and this seems to decrease drastically with increasing atomic number of the product nucleus. Because of the smaller excitation energy and hence

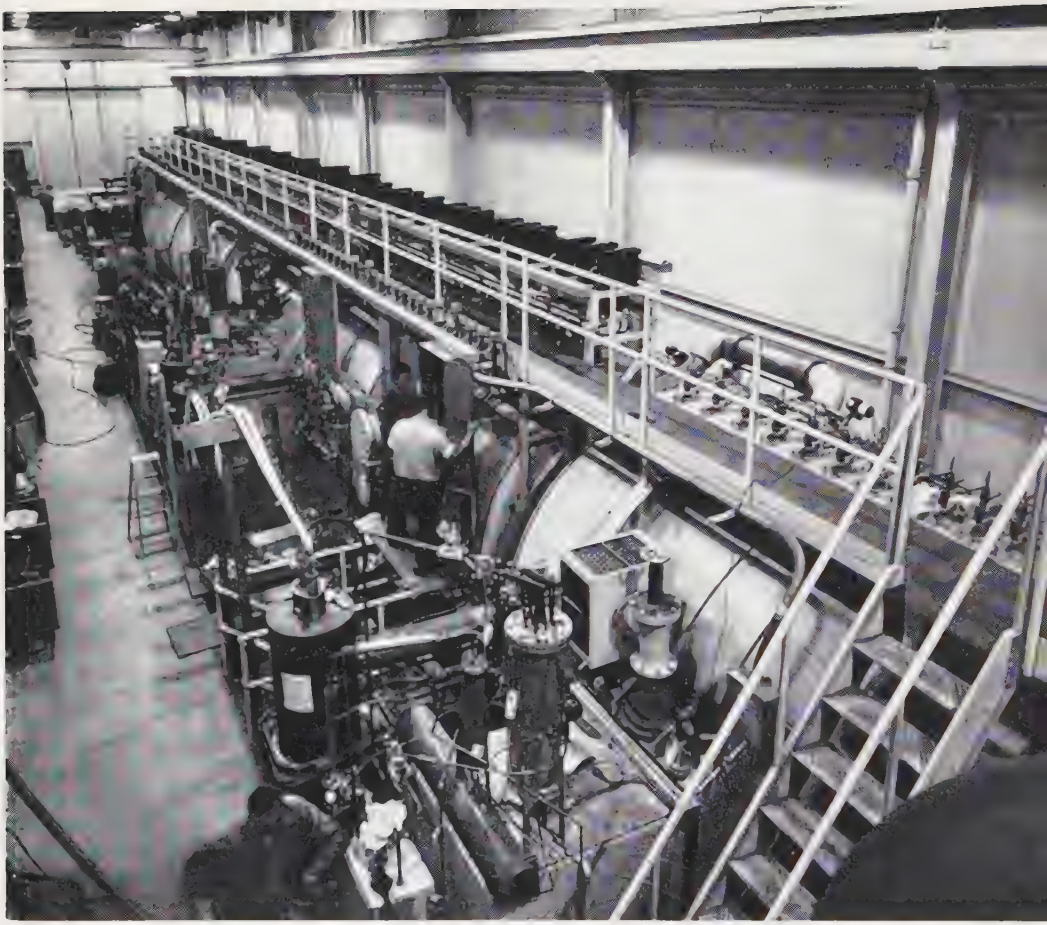


Fig. 4.10 Photograph of University of California Heavy Ion Linear Accelerator (Hilac).

the fewer chances for fission to compete, the lighter the projectile and hence the higher the atomic number of the target nucleus, the better the situation for the production of a given product nucleus, given equal beam intensities and amount of target material; however, the larger beams available for the lighter projectile and the smaller amounts of material available for the higher atomic number target material must be taken into account in the process of determining the optimum reaction in any particular case.

The prevalence of direct interaction mechanisms—which lead to spallation products because the high energy of the outgoing particles leaves the spallation product in such a low degree of excitation that it more often escapes fission—is found in deuteron and helium-ion induced reactions on the transuranium elements, as described in Section 3.1b, above. A similar mechanism might lead to some slight degree of circumvention of fission in the case of heavy-ion projectiles. For example, in a reaction such as $_{96}Cm^{244} + {}_{14}Si^{28} \rightarrow 103^{258} + {}_{7}N^{14}$, perhaps in a small but not negligible proportion of the reactions a large part of the energy is carried off by the N^{14}, leaving the 103^{258} nucleus in a sufficiently low degree of excitation to escape the fission reaction with some appreciable probability. Future work with heavy ions will undoubtedly lead to information which will enable us to understand the probability for such reactions or other reaction mechanisms which have not yet been conceived.

In summary, we can see that the synthesis and identification of future synthetic elements present a real challenge. By the time elements 104 and 105 are reached, we shall probably find that the longest-lived isotopes which can be made will exist barely long enough to permit traditional chemical identification. We can be quite sure that we shall be relying entirely on isotopes containing odd nucleons to make such chemical identifications, if these are possible at all for such high atomic numbers. It is likely that the present criteria and basic requirements for the discovery of a new element, namely complete chemical identification and separation from all previously known elements, will have to be changed at some point. Careful measurements of decay properties and determination of complete excitation functions and reaction mechanisms and the

clever use of recoil techniques with the chemical identification of daughter isotopes should make it possible to make effective and satisfactory identification of isotopes with very short half-lives. The decay properties may have to be measured at the target area, on recoil-product nuclei, during the bombardment. Reasonable, direct chemical (or equivalent) identification of the new element isotope can probably be made in some cases by using simple and fast methods involving migration of gaseous atoms or ions, volatility properties, reactions with surfaces, or gas-flow reactions. The identification of the first isotopes of all the new elements that will be discovered from now on probably will be accomplished through the use of such methods, and the production of isotopes of these new elements with sufficiently long half-lives to allow chemical identification by traditional methods, if possible at all, will follow later. Whichever method is used, acceptable evidence for the discovery of new transuranium elements should consist of reasonable establishment of the atomic number and *this demands more than the observation of predicted decay properties and yields*. Only the future can tell us if it will be necessary to settle for less than this criterion when the production of elements substantially farther up the atomic number scale is under investigation some years from now.

Appendix

Radioactive Decay Properties of Transuranium Nuclides

ISOTOPE	HALF LIFE	MODE OF DISINTEGRATION[a]	FORMATION
Neptunium			
Np^{231}	~50 m	α (6.28)	$U^{238}(d,9n)$
			$U^{235}(d,6n)$
Np^{232}	~13 m	E.C.	$U^{233}(d,3n)$
Np^{233}	35 m	E.C. (>99%)	$U^{235}(d,4n)$
		α (10^{-3}%)(5.53)	
Np^{234}	4.4 d	E.C. (>99%)	$U^{235}(d,3n)$
		β^+ (4.6×10^{-2}%)(0.8)	
Np^{235}	410 d	E.C. (>99%)	$U^{235}(d,2n)$
		α (1.2×10^{-3}%)(5.06)	
Np^{236}	>5000 y		$U^{238}(d,4n)$
Np^{236m}	22 h	β^- (57%)(0.52, 0.48)	$U^{238}(d,4n)$
		E.C. (43%)	$Np^{237}(n,2n)$
Np^{237m_2}	5.4×10^{-9} sec	I.T.	U^{237} β^- decay
Np^{237m_1}	6.3×10^{-8} sec	I.T.	Am^{241} α decay
			U^{237} β^- decay
Np^{237}	2.20×10^6 y	α (4.787, 4.767 plus others ranging from 4.87 to 4.52)	U^{237} β^- decay
		β stable	
Np^{238}	2.10 d	β^- (1.25, 0.28, 0.25)	$U^{238}(d,2n)$
			$Np^{237}(n,\gamma)$
Np^{239}	2.35 d	β^- (0.64, 0.43, 0.33, 0.21)	U^{239} β^- decay
Np^{240m}	7.3 m	β^- (2.16, 1.59, 1.26, 0.76)	U^{240} β^- decay
Np^{240}	63 m	β^- (0.9)	$U^{238}(\alpha,pn)$
Np^{241}	~3.4 h	β^-	
Plutonium			
Pu^{232}	36 m	E.C. (≤98%)	$U^{235}(\alpha,7n)$
		α (≥2%)(6.58)	
Pu^{233}	20 m	E.C. (>99%)	$U^{233}(\alpha,4n)$
		α (0.1%)(6.30)	
Pu^{234}	9 h	E.C. (94%)	$U^{235}(\alpha,5n)$
		α (6%) (6.19)	Cm^{238} α decay
Pu^{235}	26 m	E.C.	$U^{235}(\alpha,4n)$
		α (3×10^{-3}%)(5.85)	
Pu^{236}	2.85 y	α (5.763, 5.716, 5.610, 5.448)	$U^{235}(d,n)$
		β stable	Cm^{240} α decay
Pu^{237m}	0.18 sec	I.T.	Cm^{241} α recoils
Pu^{237}	45.6 d	E.C. (>99%)	$U^{238}(\alpha,5n)$
		α (3.3×10^{-3}%)(5.65, 5.36)	$U^{235}(\alpha,2n)$

ISOTOPE	HALF LIFE	MODE OF DISINTEGRATION[a]	FORMATION
Pu^{238}	86.4 y	α (5.495, 5.452 plus others ranging from 5.35 to 4.61) β stable	$U^{238}(d,2n)$ Cm^{242} α decay $Np^{237}(n,\gamma)Np^{238}$ $\xrightarrow{\beta^-}$
Pu^{239m_2}	1.93×10^{-7} sec	I.T.	Cm^{243} α decay Np^{239} β^- decay
Pu^{239m_1}	1.1×10^{-9} sec	I.T.	Cm^{243} α decay Np^{239} β^- decay
Pu^{239}	24,360 y	α (5.147, 5.134 plus others ranging from 5.10 to 4.66) β stable	Np^{239} β^- decay
Pu^{240}	6,580 y	α (5.159, 5.115 plus others ranging from 5.01 to 4.85) β stable	$Pu^{239}(n,\gamma)$
Pu^{241}	13.0 y	β^- (>99%)(0.0205) α (3×10^{-3}%)(4.893, 4.848)	$Pu^{240}(n,\gamma)$
Pu^{242}	3.73×10^5 y	α (4.898, 4.854) β stable	$Pu^{241}(n,\gamma)$
Pu^{243}	4.98 h	β^- (0.58, 0.49, 0.37)	$Pu^{242}(n,\gamma)$
Pu^{244}	7.6×10^7 y	α β stable	$Pu^{243}(n,\gamma)$
Pu^{245}	10.1 h	β^-	$Pu^{244}(n,\gamma)$
Pu^{246}	10.85 d	β^- (0.33, 0.15)	$Pu^{245}(n,\gamma)$
Americium			
Am^{237}	1.3 h	E.C. (99%) α (5×10^{-3}%)(6.01)	$Pu^{239}(d,4n)$
Am^{238}	1.86 h	E.C.	$Pu^{239}(d,3n)$
Am^{239}	12 h	E.C. (>99%) α (4.1×10^{-3}%)(5.78)	$Pu^{239}(d,2n)$
Am^{240}	50 h	E.C.	$Pu^{239}(d,n)$
Am^{241}	458 y	α (5.476, 5.433 plus others ranging from 5.54 to 5.24) β stable	Pu^{241} β^- decay
Am^{242m}	16.01 h	β^- (81%)(0.667, 0.625) E.C. (19%) I.T. $\leq$ 6%	$Am^{241}(n,\gamma)$
Am^{242}	~100 y	β^- (90%)(0.585) E.C. (10%)	$Am^{241}(n,\gamma)$
Am^{243}	7950 y	α (5.267, 5.224 plus others ranging from 5.340 to 5.169) β stable	$Am^{242}(n,\gamma)$ Pu^{243} β^- decay
Am^{244}	26 m	β^- (>99%)(1.5) E.C. (3.9×10^{-2}%)	$Am^{243}(n,\gamma)$
Am^{245}	1.98 h	β^- (0.905)	Pu^{245} β^- decay
Am^{246}	25 m	β^- (2.10, 1.60, 1.35)	Pu^{246} β^- decay
Curium			
Cm^{238}	2.5 h	E.C. (<90%) α (>10%)(6.50)	$Pu^{239}(\alpha,5n)$
Cm^{239}	~3 h	E.C.	$Pu^{239}(\alpha,4n)$

ISOTOPE	HALF LIFE	MODE OF DISINTEGRATION[a]	FORMATION
Cm^{240}	26.8 d	α (6.25, 6.21)	$Pu^{239}(\alpha,3n)$
Cm^{241}	35 d	E.C. (99%) α (1%)(5.95, 5.90)	$Pu^{239}(\alpha,2n)$
Cm^{242}	162.5 d	α (6.110, 6.066 plus others ranging from 5.97 to 5.19) β stable	$Pu^{239}(\alpha,n)$ Am^{242} β^- decay
Cm^{243}	35 y	α (>99%)(5.780, 5.736 plus others ranging from 6.061 to 5.58) E.C. (0.3%)	$Cm^{242}(n,\gamma)$
Cm^{244}	19 y	α (5.801, 5.759, 5.661, 5.515) β stable	$Cm^{243}(n,\gamma)$ $Am^{243}(n,\gamma)Am^{244} \xrightarrow{\beta^-}$ Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cm^{245}	1.4×10^4 y	α (5.45, 5.36) β stable	$Cm^{244}(n,\gamma)$ Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cm^{246}	5000 y	α (5.37) β stable	$Cm^{245}(n,\gamma)$ Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cm^{247}	$\geq 4 \times 10^7$ y	α β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cm^{248}	4.7×10^5 y	α (5.054) S.F. (10%) β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cm^{249}	65 m	β^- (0.9)	$Cm^{248}(n,\gamma)$ Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cm^{250}	2×10^4 y	S.F. β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Berkelium			
Bk^{243}	4.5 h	E.C. (>99%) α (0.15%)(6.72, 6.55, 6.20)	$Am^{241}(\alpha,2n)$
Bk^{244}	4.4 h	E.C. (>99%) α (6×10^{-3}%)(6.67)	$Am^{241}(\alpha,n)$

ISOTOPE	HALF LIFE	MODE OF DISINTEGRATION[a]	FORMATION
Bk^{245}	4.95 d	E.C. (>99%) α (0.1%)(6.37, 6.17, 5.89)	$Am^{243}(\alpha,2n)$
Bk^{246}	1.9 d	E.C.	$Am^{243}(\alpha,n)$ $Cm^{244}(\alpha,pn)$
Bk^{247}	7×10^3 y	α (5.67, 5.50, 5.30)	Cf^{247} E.C. decay $Cm^{244}(\alpha,p)$
Bk^{248}	16 h	β^- (70%)(0.65) E.C. (30%)	$Bk^{247}(n,\gamma)$ $Cm^{245}(\alpha,p)$ $Cm^{246}(\alpha,pn)$
Bk^{249}	290 d	β^- (>99%)(0.10) α (10^{-3}%)(5.40, 5.08)	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Bk^{250m}	3.9×10^{-8} sec	I.T.	E^{254} α decay
Bk^{250}	3.13 h	β^- (1.9, 0.9)	$Bk^{249}(n,\gamma)$
Californium			
Cf^{244}	25 m	α (>99%)(7.17) E.C. (?)	$Cm^{242}(\alpha,2n)$
Cf^{245}	44 m	E.C. (66%) α (34%)(7.11)	$Cm^{242}(\alpha,n)$ $Cm^{244}(\alpha,3n)$
Cf^{246}	35.7 h	α (6.753, 6.711, 6.615, 6.467) β stable	$Cm^{244}(\alpha,2n)$
Cf^{247}	2.4 h	E.C.	$Cm^{244}(\alpha,n)$
Cf^{248}	350 d	α (6.26) β stable	$U^{238}(N^{14},p3n)$ $Cm^{245}(\alpha,n)$
Cf^{249}	400 y	α (5.806 plus others ranging from 6.19 to 5.57) β stable	Bk^{249} β^- decay
Cf^{250}	9.3 y	α (6.024, 5.980) β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture Bk^{250} β^- decay
Cf^{251}	660 y	α β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cf^{252}	2.2 y	α (97%)(6.112, 6.069, 5.970) S.F. (3%) β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cf^{253}	19 d	β^- (0.27)	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Cf^{254}	56 d	S.F. β stable	E^{254} E.C. decay Pu^{239} multiple neutron capture

ISOTOPE	HALF LIFE	MODE OF DISINTEGRATION[a]	FORMATION
Cf^{254}			U^{238} multiple neutron capture
Einsteinium			
E^{246}	7.3 m	E.C. α (7.35)	$U^{238}(N^{14},6n)$
E^{248}	25 m	E.C. (>99%) α (0.3%)(6.87)	$Cf^{249}(d,3n)$
E^{249}	2 h	E.C.(>99%)α(0.1%)(6.76)	$Bk^{249}(\alpha,4n)$
E^{250}	8 h	E.C.	$Bk^{249}(\alpha,3n)$ $Cf^{249}(\alpha,p2n)$ $Cf^{249}(\alpha,3n)Fm^{250} \xrightarrow{E.C.}$
E^{251}	1.5 d	E.C. (99.5%) α (~0.5%)(6.48)	$Bk^{249}(\alpha,n)$
E^{252}	~140 d	α (6.64)	$Bk^{249}(\alpha,n)$
E^{253}	20.0 d	α (6.633, 6.592 plus others ranging from 6.55 to 6.17) β stable	Cf^{253} β^- decay Pu^{239} multiple neutron capture U^{238} multiple neutron capture
E^{254m}	36 h	β^- (99.9%)(1.04, 0.381) E.C. (~0.1%)	$E^{253}(n,\gamma)$ Pu^{239} multiple neutron capture U^{238} multiple neutron capture
E^{254}	280 d	α (6.44)	$E^{253}(n,\gamma)$ Pu^{239} multiple neutron capture U^{238} multiple neutron capture
E^{255}	40 d	β^-	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
E^{256}	hour or less	β^-	$E^{255}(n,\gamma)$
Fermium			
Fm^{250}	~0.5 h	α (7.43)	$Cf^{249\text{-}252}(\alpha,xn)$ $Cm^{244}(C^{12},\alpha 2n)$ $U^{238}(O^{16},4n)$
Fm^{251}	7 h	E.C. (99%) α (~1%)(6.89)	$Cf^{249}(\alpha,2n)$
Fm^{252}	23 h	α (7.04) β stable	$Cf^{249\text{-}252}(\alpha,xn)$ $Cf^{250}(Be^{9},\alpha 3n)$
Fm^{253}	~4.5 d	E.C. (90%) α (10%)(6.94)	$Cf^{249\text{-}252}(\alpha,xn)$
Fm^{254}	3.24 h	α (7.20, 7.16, 7.06) S.F. (0.06%) β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture

ISOTOPE	HALF LIFE	MODE OF DISINTEGRATION[a]	FORMATION
Fm^{254}			E^{254m} β^- decay
Fm^{255}	22 h	α (7.03) β stable	Pu^{239} multiple neutron capture U^{238} multiple neutron capture
Fm^{256}	~3 h	S.F.	$E^{255}(n,\gamma)E^{256} \xrightarrow{\beta^-}$
		β stable	$E^{253}(\alpha,n)Mv^{256} \xrightarrow{\text{E.C.}}$ $E^{253}(\alpha,p)$
Mendelevium			
Mv^{256}	~1/2 h	E.C.	$E^{253}(\alpha,n)$
102			
102^{254}	~3 s	α (~8.5 est.)	$Cm^{246}(C^{12},4n)$

[a] Energy of radiation in million electron volts; E.C. = electron capture; I.T. = isomeric transition; S.F. = spontaneous fission.

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